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A STUDY OF LITHOGRAPHIC INK AND WATER INTERACTIONS

DENNET CHAMBERS

**A thesis submitted in partial fulfilment of the requirements
of the Open University for the degree of Doctor of Philosophy**

December 1994

Sponsoring establishment:

The London Institute: London College of Printing & Distributive Trades, SE1 6SB

Collaborating establishment:

Pira International, Leatherhead, Surrey, KT22 7RU

Author number: A9255262
Date of submission: December 1994
Date of award: 30 January 1995

Associated Studies

Additional studies to the subject area and related aspects include:

- i) Attendance and participation in a number of relevant conferences meetings and seminars**
- ii) Poster presentation at the Second British Colloid & Surface Science Student meeting, University of Nottingham, April 1993.**

Acknowledgements

I would like to express my gratitude to Professor D J Morantz, Mr J W Birkenshaw and Dr A Manning for having faith in me and giving me the opportunity to carry out this study. Additionally, I would like to thank Professor Morantz, the director of the project for his assistance and guidance over the last few years. I am grateful to Dr A Manning for providing advice, support and a study base at the college which I have used over the last year.

I would like to thank John Birkenshaw, the head of the Print Process group, for making me feel part of the team at Pira International and for his help in providing the equipment and space necessary for this study to be carried out.

I am indebted to the following people for providing materials, equipment, advice and facilities during this study: Mr T Boutle (DSM), Dr S Taylor and Dr J Clint (BP Sunbury) and Mr G Etherington and Mr C Warren (Roth Scientific).

I would like to thank my friends and colleagues at Pira for making my stay so pleasant, particularly Ruby Arora for our mutually beneficial 'brain-storming sessions' and also Amru Saxena and Michael Mallouris who together with Ruby proved to be firm friends.

I am grateful to Dr C Parsons for the use of the computing facilities at the college and also to Miss S Johnson for her valuable assistance and friendship. Additionally, I would like to thank Mrs S Riablershirun and Dr W Sananpanichkul for their friendship, assistance and support throughout these studies.

Finally, I would like to thank those closest to me for their support and encouragement during this challenging period of my life. I am grateful for the quiet but constant support of my family. I am particularly indebted to Andrew Gardner and Pam Sehmi for their love, friendship, support and assistance over and beyond the course of this study. I could not have done it without you.

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A STUDY OF LITHOGRAPHIC INK AND WATER INTERACTIONS

ABSTRACT

Achieving and maintaining the correct ink/water balance is crucial for acceptable print quality; this involves factors affecting the emulsification of water and ink. This process was investigated with two designed model ink varnishes (one being 'hydrophilic' relative to the other 'hydrophobic' varnish) and two commercial varnishes. The Surland test, widely used to characterise ink/water balance, showed differences in water uptake between inks and corresponding varnishes; however it did not distinguish between the 'hydrophilic' and 'hydrophobic' systems. Thus, the rheology of the systems are considered together with implications to the lithographic process.

Rheological studies of creep and flow showed that the hydrophilic and hydrophobic systems behaved differently in the presence of water. The rheology of the ink varnish plays a major role in emulsification and the nature of processes at the interface affecting droplet fragmentation, droplet coalescence and time-dependency. Slippage occurred in the hydrophobic systems to a greater extent compared with the hydrophilic systems increasing with water concentrations from 0 to 25% water.

Droplet size distributions of the emulsion depend on temperature and agitation speeds. As emulsions approached dynamic equilibria, mean droplet diameters in the hydrophobic varnish at 70°C and 40°C were found to be ca. 25 and 12 μm respectively; corresponding mean droplet diameters in the hydrophilic varnish were ca. 20 μm and 5 μm . Increase of interfacial tension for both varnishes (ca. 6 mNm^{-1}) between 40°C and 70°C, may not be significant to droplet breakdown. A reduction in viscosity i.e. from 100 to 5 Pas in the hydrophobic varnish and from 300 to 5 Pas for the hydrophilic varnish was the determining factor. Droplet size depends on temperature: e.g. temperature increases led to larger droplets. Viscosity ratios of the continuous and disperse phases account for these effects.

Investigating the time-dependency of the system showed that allowing 'rest periods' between episodes of mixing altered the rate and nature of emulsification. Thus using a modified varnish, rest periods of 1 and 3 minutes produced mean droplet diameters in the range of 1.5-1.8 μm whereas a rest period of 5 minutes produced diameters of 2.3-2.4 μm indicating that thixotropic recovery which occurs up to 3 minutes, restores the rate of droplet breakdown; whereas, after 5 minutes, coalescence is dominant. Extending the 'rest period' allows time for drainage of a film of continuous phase between two colliding droplets. These time-dependent effects varied with different varnish modifications. The effect of IPA on emulsification was also time-dependent. During 3 minutes of stirring at 900 rpm, the number of droplets below 2 μm was greater in an emulsion containing IPA than in one containing water only; the situation was reversed after 4 minutes of stirring where the number of droplets below 2 μm was lower. A decrease in interfacial viscosity at the varnish/water interface is considered; such a decrease may reduce the effective shear stress at the interface and thus the extent of droplet breakdown.

Aims and Objectives

The aim of this study is to investigate the factors affecting the formation of water-in-ink emulsions in lithography. In order to conduct a detailed study, the literature concerning emulsification and rheology is reviewed and two model ink varnishes of differing degrees of hydrophobicity are designed.

These materials will be evaluated by the Surland emulsification method, modifications of this test and rheological assessment. The response of droplet size distribution to changes in rheology (including temperature effects) are to be examined optically and interfacial tensions of these emulsions will be investigated.

The evaluation of these properties will enable other aspects affecting emulsification - including agitation speed, memory effects and the addition of isopropyl alcohol to the fountain solution - to be examined.

I INTRODUCTION AND BACKGROUND

1. Introduction

1.1 The lithographic process

The subject of ink/water interactions in lithography has been of interest to the printing and ink industries for some years¹. Offset lithographic printing is a planographic process where the image and non-image areas are held within the same plane. Offset lithography differs from other processes in that the image is not transferred directly from the printing plate to the substrate; instead the image is offset onto a printing blanket which then transfers the image onto the substrate.

The technology upon which the lithographic printing process is based uses the fact that oil and water do not form a solution. The printing plates are chemically treated so that the image areas are hydrophobic/lyophilic whereas the non-image areas are hydrophilic. A light-sensitive coating on the plate enables the image to be formed photographically. For example, in negative-working plate making, exposure to ultraviolet light causes the image areas to become cross-linked, giving rise to a hydrophobic/lyophilic surface. The unexposed polymer is then removed thus revealing the hydrophilic surface of the plate.

The plate is dampened with a 'fountain' solution consisting of approximately 98% water; this forms a continuous film across the non-image area and acts as a physical barrier to the ink. However, the high contact angle of the water in relation to the image area prevents the overall formation of a continuous film of water; hence the water retracts into fine droplets on the image areas. When ink is applied to the plate it is repelled by the water-coated non-image areas and accepted by the image areas.

While the mutual rejection of water and ink is vital to the process, it is necessary for the ink to emulsify some of the water droplets from the image areas of the plate. It is important that the ink should retain its physical properties and maintain its print

performance during this process. Establishing an appropriate balance of ink and water in lithography is a most important factor in producing an acceptable image.

This study is concerned with lithographic inks, which are dispersions of pigment in a solution of resins dissolved in a petroleum distillate², and the subsequent emulsion formed when water droplets are dispersed within the ink.

1.2 Colloidal systems

The term colloid is used to describe an intermediate class of materials lying between bulk and molecularly dispersed systems. Colloidal systems consist of a dispersed phase (or discontinuous phase) distributed in a finely divided state in a dispersion medium (or continuous phase). A system may be defined as being in a colloidal state when the dimensions of the disperse phase lie in the range of 1-1000 nm³. Below the lower limit of 1 nm, colloid behaviour merges into that of molecular solutions. In the simplest colloids a distinction can be made between the disperse phase and the dispersion medium. However, more complex colloidal dispersions exist where several phases co-exist, these are termed multiple colloids. Examples of colloidal systems are aerosols, emulsions, sols, gels, foams and solid dispersions.

Colloidal dispersions can be formed by either breaking down bulk matter to colloidal dimensions (i.e. by dispersion) or by building up molecular aggregates to colloidal dimensions (i.e. by condensation or nucleation).

The dispersion methods which are of relevance to this study may be separated into two groups; i.e. comminution and emulsification. The comminution process involves grinding solid materials into particles of colloidal dimensions; this is particularly important in the manufacture of all inks. The ink is passed through a three roll mill in order to break up aggregates of pigment particles. Emulsions and emulsification will be discussed in section 1.2.2.

Many colloidal dispersions are of practical importance e.g. foodstuffs, pharmaceuticals, rubber, inks and paints. In addition, there are many processes which rely heavily on the application of colloid phenomena e.g. detergency, lubrication, emulsion polymerisation and oil-well drilling^{3,4}.

1.2.1 Colloid stability

The creation of a colloid system results in a large increase in surface to volume ratio as particles or droplets are dispersed⁵. A significant proportion of molecules will therefore be associated with the microheterogeneous regions which form the interfaces between the dispersed phase and continuous phase. These molecules will contribute to the thermodynamic properties of the system in a different manner from those molecules in the bulk phases. The presence of the interface will therefore affect the overall thermodynamic state of the system and in particular its free energy.

The separation of bulk molecules into smaller pieces or particles results in an increase of surface and an increase in the potential energy of the system. This may be regarded as a measure of the work done (ΔW) to give separation; if this process is carried out isothermally, then this is equal to the increase in free energy, ΔG . However, the increase in the free energy is dependent upon the distance between the separated particles. The surface molecules are still under the influence of the opposing faces. When the particles are an infinite distance apart, the increase in free energy is proportional to the area of the surface created ($2A$) and is called the surface excess free energy, thus

$$\Delta G = \Delta W = 2A\gamma^0 \quad (1)$$

where γ^0 is the surface or interfacial tension.

If the above separation should take place in a vacuum, the forces of attraction will have an influence at all separations, with the free energy of the system decreasing as the distance

between the particles becomes smaller. However, if the separation takes place in the presence of a pure liquid, the space between the particles is filled with the liquid. The forces of attraction between the particles may therefore be reduced.

The presence of a liquid medium that is not pure may enhance the repulsive force between the separated particles. If such a force exists, work must be done to bring the particles closer together; therefore as the separation decreases the free energy arising from the repulsion increases.

The forces of attraction and repulsion are additive and therefore contribute to the total free energy of a colloid system. A colloid system will remain stable if the repulsive forces are large enough to prevent the recombination of particles or droplets.

Colloidal dispersions represent states of higher free energy than that of the corresponding material in bulk and can be regarded as being thermodynamically unstable³. Therefore, a most important physical property of colloidal dispersions is the tendency of particles to aggregate. According to the laws of thermodynamics, passage to a state of lower free energy will therefore occur spontaneously. However, if a substantial energy barrier exists which prevents the elimination of the colloidal state, then the dispersion is said to be at a metastable equilibrium. If conditions are altered and the energy barrier becomes either negligibly small or is totally removed, then the colloid becomes unstable^{3,4}.

It can be seen that the stability and preparation of colloids is associated with the presence of a free energy barrier of sufficient height to prevent the breakdown of the colloid state. Conversely, the problems of destruction of colloid dispersions will be dependent upon the ability to reduce, remove or surpass the energy barrier. While the range of possible colloidal systems is vast, their existence may be undesirable. Therefore it is important to know how to create and how to destroy them.

For colloidal dispersions, the energy which would be necessary to carry a system over the energy barrier comes from the Brownian motion of the particles. This occurs as a result of the random bombardment of the surface of the dispersed particles by the molecules of the continuous phase. The average translational energy of colloidal particles undergoing Brownian motion is of the order of $(3/2)kT$ per particle where k is the Boltzmann constant, $(1.38 \times 10^{-23} \text{ J molecule}^{-1}\text{K}^{-1})$ ⁶, and T is the absolute temperature. Two particles at 300K will contribute energy of the order of 10-20 J to a collision. However, at a given moment a particle may have a larger or smaller energy. Hence, the chances of a collision involving several times kT (e.g. $10kT$) is greatly reduced. Therefore, if the free energy barrier is sufficiently high, compared with kT , the dispersion will remain indefinitely in a metastable state. Such a dispersion is said to be colloiddally stable^{4,5}.

Instability will occur if the height of the free energy barrier is reduced³ to the order of $1-2kT$. This will result in the tendency for the colloid to return to its bulk components, taking various forms.

It is clear from the above discussion that the stability of colloids relies upon creating and maintaining the free energy barrier. In addition to the intermolecular and interparticle forces that are present in any system and the electrostatic repulsion forces that may be present in ionic systems, the stability of a colloid may be increased by introducing substances that increase the energy barrier. These substances will be discussed with reference to emulsion stability in section 1.2.2.

1.2.2 Emulsions

An emulsion is a colloidal system in which both the dispersed phase and the dispersion medium are liquids. Generally, one of the liquids^{3,4} is water or an aqueous medium and the other is an oil or some other water immiscible liquid. With a given pair of liquids (e.g. oil and water) two distinct types of emulsion are possible according to which forms the dispersion medium. Emulsions in which an oil is dispersed in water are termed oil-in-

water (o/w) emulsions. Emulsions in which the water is the dispersed phase are referred to as water-in-oil (w/o) emulsions. In general, an o/w emulsion has a creamy texture (e.g. milk) and a w/o emulsion has a greasy texture (e.g. butter). Emulsions may be further classified according to the size of the dispersed droplets. The term microemulsion is used to describe emulsions where the dispersed particles are 0.01-0.1 μm in diameter⁵. Where the diameter is in excess of this, emulsions may be referred to as macroemulsions.

A most important physical property of a colloidal dispersion is its stability. The results of instability in emulsions are creaming, coagulation and coalescence where the emulsion is broken down. Creaming occurs as a result of a density difference between the two phases. Droplet collisions may lead to coalescence into larger droplets. Eventually, this may lead to complete phase separation where a single interface separates the dispersion medium and the other phase.

If an emulsion is prepared by homogenising two pure liquid components, phase separation will usually be rapid. In order to prepare a reasonably stable emulsion, it may be necessary to use an emulsifying agent.

The materials which are most effective as emulsifying agents can be broadly classified into three main groups: surface active agents; finely divided solids; and naturally occurring materials⁴. Surface active materials are usually more soluble in one phase; according to Bancroft's rule, the phase in which the emulsifying agent is more soluble tends to be the dispersion medium. Finely divided solids are preferentially wetted either by an oil or aqueous phase. Naturally occurring materials such as proteins stabilise emulsions by providing mechanical protection at the interfaces. Solids that are preferentially wetted by water tend to give o/w emulsions whereas those solids wetted by oil tend to give w/o emulsions.

The function of an emulsifying agent is to facilitate emulsification and promote emulsion stability^{3,5}. The emulsifying agent forms an adsorbed film around the dispersed droplets

which helps to prevent coagulation and coalescence. Emulsifying agents impart various properties upon the emulsion which increases its stability. For example, the adsorption of surfactant at the oil-water interface causes a lowering of interfacial energy, thus facilitating the development of, and enhancing the stability of the large interfacial areas associated with emulsions. Interparticle repulsions may be introduced to the system by means of ionic emulsifying agents; this is a particularly useful means of stabilising o/w emulsions.

1.3 Lithographic inks

The mechanisms involved in the definition of image and non-image areas by the ink and fountain solution impose chemical and physical restrictions on lithographic inks, the details of which are given below.

In order to achieve controlled emulsification, lithographic inks are generally produced at relatively high viscosities. The combination of a high viscosity ink with a low viscosity fountain solution, together with a limited mutual affinity, has consequences for the degree of emulsification².

A further consequence of the viscosity of these inks is that a substantial amount of mechanical work is required to deliver a thin, even film of ink to the printing plate. In order to achieve this, the ink is passed through a long series of distribution rollers consisting of alternating metal and elastomeric-surfaced rollers. The use of elastomers on some rollers provides further restrictions on the nature of solvents included in the formulation of lithographic inks. Elastomeric materials are prone to solvent attack which can result in the softening and swelling of the rollers' surfaces, thus producing uneven ink films. The use of strong solvents must therefore be avoided.

In addition, the solvents used must be of low volatility^{1,2}. The mechanical work done on the ink as it passes through the roller system results in the generation of heat. This factor,

combined with the exposure of ink at a high surface to volume ratio throughout the roller distribution train, would lead to the evaporation of volatile solvents from the ink.

The composition of lithographic inks is therefore limited by the need to obtain a balance between suitable materials and process requirements.

1.3.1 Lithographic ink composition

Lithographic inks essentially consist of three groups of components: pigments; resins/vehicles; and solvents. However, various additives can also be included which may modify certain runnability and print performance characteristics of the basic pigment, resin and solvent combinations².

1.3.2 Pigments

In lithography, a thin film of 1 to 3 microns in thickness is delivered to the substrate. It is this factor which places limitations on the basic nature of pigments suitable for use in lithography. The pigments used must have a high tinctorial strength, thereby giving maximum coverage at relatively low concentrations^{2,7,8}. The particles must also be finely dispersed in the vehicle^{9,10}, with the particle size not exceeding that of the final printed ink film thickness. The inclusion of these fine particles must not cause any undue increases in viscosity, yield or thixotropy which would affect the mobility of the ink on the press. Given the nature of the lithographic process, it is vital that the pigment does not dissolve in, or react with, the aqueous fountain solution⁸.

In order to incorporate pigment particles into an ink, the surface of the pigment must be wetted by an appropriate medium which can then be incorporated into the varnish. Good pigment wetting is essential for satisfactory ink rheology and transference. Ideally, individual or primary pigment particles should be wetted and sterically stabilised by long chain alkyds that are used in the vehicle, thus preventing aggregation or flocculation of

the pigment particles. Although the surface of the pigment particle has polar moieties, it is preferentially oleophilic and is sufficiently wetted by the vehicle⁷.

1.3.3 Resins/vehicles

Lithographic ink vehicles can be divided into two major classes. Firstly, there are the oleoresinous systems containing both hard resin and drying oil alkyd which are used to produce quick set, heat set and oxidation drying inks². Secondly, there are the acrylate systems used in ultraviolet curable inks. The former system will be discussed here.

The resins used in lithographic inks must be soluble in weak solvents (the nature of which is discussed in section 1.3.4). Also, the resin must have a controlled tolerance to water in that it must be neither water miscible nor totally water repellent. These requirements limit the choice of resins available for use in lithographic inks. The hard resins used tend to fall into two categories: modified hydrocarbons or modified rosin ester groups of resins. Examples of such chemical modifications of the latter are maleic and phenolic derivatives. The two types of resins may be combined in specified proportions to achieve particular water uptake characteristics. This is possible because the hydrocarbon resins are more water repellent than the rosin esters which have acid groups that impart a degree of water tolerance to the system.

The press stability of the inks is largely dependent upon the solvency of the resins in the varnish. The molecular weight of the resins will have an effect on the degree of solvency. Lower molecular weight resins will generally give greater solvency. A resin with low solvency in the varnish will have low shear stress stability and will therefore break down as the speed of the press is increased. Ideally, the resins should have sufficient solubility, for maximum stability, coupled with a rapid viscosity rise during solvent release in order to give the fastest possible setting².

The chemical modifications and molecular varieties which are available can have a marked influence on printability and print characteristics. One of the primary properties that can be altered is the solubility or compatibility of the resin. However, the compatibility of a vehicle is not controlled by resin type alone, it may be influenced by the types and proportions of oils and solvents.

The drying oil/alkyd is essentially a liquid resin which acts as a solubiliser and 'binder' for the hard resins.

The ratio of oil to resin affects the performance of the varnish. For example, a high oil to resin combination minimises compatibility and promotes setting at the expense of good stability. The oil and resin content must be balanced to meet specific applications, for example, a high speed heat set ink would require a high resin to oil ratio.

In addition to the above, the drying oil contributes to the water absorbance and film forming properties of the ink.

1.3.4 Solvents

The choice of solvents suitable for use in lithographic inks is limited by the constraints imposed by the lithographic process. The volatility and solvency restrictions placed upon the distillates mean that only high boiling point petroleum fractions with weak solvent power are suitable^{1,2}.

The major properties of the petroleum distillates are their boiling point range and aromatic content. The boiling ranges are generally narrow in order to achieve the optimum balance between press stability and phase separation. A broader boiling range can lead to poor stability due to the evaporation of the more volatile, lower boiling point fractions from the ink distribution rollers. It is also possible that slower setting times can occur as a result of the retention of poorly mobile high-boiling fractions. The aromatic content of the

distillate determines its degree of solvency, i.e. an increase in aromatic content gives greater solvent power. Different solvents may be blended together in order to obtain the correct solvency balance.

A certain amount of distillate is also used for the adjustment of the rheological properties of the varnish at the end of production.

1.3.5 Additives

A wide range of additives are used in small proportions to modify the printability and other characteristics of the ink². Driers may be added to accelerate the drying process by encouraging cross-linking of the drying oils during oxidation. These driers are derived from transition group metals whose catalytic action arises as a result of repeated transitions from one oxidation state to another e.g. cobalt (II) to cobalt (III).

Waxes are incorporated into an ink to provide slippage between the rollers as it passes through the nip and also to impart a degree of rub and scratch resistance to the dried ink film. The most widely used types of waxes in lithographic inks are: polyethylene (PE), which provides good rub and scratch resistance; and polytetrafluoroethylene (PTFE), which promotes surface slippage.

Anti-oxidants are included in the inks to delay the skinning over of inks during storage and stoppages. Several types of anti-oxidants are used in lithographic inks. Oximes e.g. methyl ethyl ketoxime, phenolic anti-oxidants, e.g. butylated hydroxytoluene (BHT) and quinones are typical anti-oxidants that are found in lithographic inks. A good balance between the drying properties of the ink and non-skinning behaviour must be achieved in formulations.

Anti-set-off compounds are used to prevent setting-off between the pages of stacks of printed material. This involves incorporating some particulate matter which has a larger

particle size than the printed ink film. These particles protrude out of the surface of the ink film and so provide a physical separation between the printed image and the sheet resting on it. Typical anti-set-off compounds are silica and starch.

The solids content of the resins in a varnish has to be limited in order to maintain stability on the press. If the rheological properties of the varnish are not acceptable it may be necessary to add a rheology modifier. Gelling agents (e.g. an aluminium soap, which is usually a high molecular weight resin) can be formulated into the ink to improve its rheological behaviour. When this material gels, an increase in network structure results in an increase in viscosity without undue effects upon the yield value and thixotropy. A further effect of the increase in structure is to impart greater water absorption characteristics upon the varnish.

A typical formulation for a heat set ink is given below (Table 1)²:

	Parts
Diarylamide yellow	15.0
Modified rosin ester }	
Modified hydrocarbon ester }	75.0
Low aromatic distillate }	
Micronised PE wax	2.0
Micronised PTFE wax	0.5
Low aromatic distillate	7.5
<hr/>	
Total	100.0

Table 1 A typical heat-set ink formulation

The formulation developed for the model varnishes is restricted to the main components above, i.e. resins, hydrocarbons and distillates.

1.4 Physical properties of lithographic inks

The transport of ink through a lithographic press and its interaction with different surfaces is controlled by its surface chemistry and rheology.

1.4.1 Surface properties

When a liquid is placed on a solid surface in the presence of a vapour phase, it forms a contact angle with the solid^{3,5} (Fig 1).

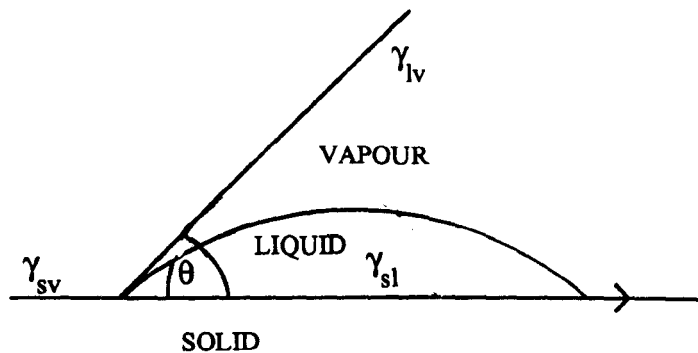


Fig 1 Relationship between solid, liquid and vapour phases

This situation at equilibrium is described by Young's equation:

$$\gamma_{sl} = \gamma_{sv} - \gamma_{lv} \cos \theta \quad (2)$$

where

γ_{sl} = Interfacial tension at the solid/liquid interface

γ_{sv} = Interfacial tension at the solid/vapour interface

γ_{lv} = Interfacial tension at the liquid/vapour interface

If the contact angle θ is less than 90° the droplet of fluid will spread on a solid surface. Moreover, as θ approaches 0° , the tendency of the fluid to spread on the solid surface increases. When θ is equal to 0° a liquid will spontaneously spread on the surface while displacing the vapour phase. Under these conditions, the fluid is said to have wetted the surface of the solid.

The transfer of the ink through the press can be more accurately described by the Young-Dupré equation which takes into account the work of adhesion between the solid and liquid phase.

$$W_a = \gamma_{lv}(1 + \cos\theta) \quad (3)$$

where W_a = work of adhesion

Consider the situation on the press where essentially two surfaces are pushed together, then pulled apart. The ink film splits every time it passes through a nip. In order for this to happen, the strength of adhesion at the solid/ink interface must be greater than the cohesive strength of the ink-ink bonds. A model put forward by Macphee (1979), assumes that the ink film splits symmetrically, however, the location of the splitting median will also be influenced by the adhesive strengths of the surfaces of the alternating chrome and elastomeric surfaces, as well as the asymmetry of air inclusions¹¹. Macphee's model is discussed in section 2.1.1

The above description refers only to the splitting of the unemulsified ink film. The introduction of fountain solution to the ink will alter the splitting pattern. This will be discussed in section 2.1.1.

1.4.2 Rheological considerations

Rheology is concerned with the flow and deformation of matter under the influence of externally applied forces^{2,12}. The simplest rheological behaviour is exhibited at one extreme by Hookean elastic solids and at the other extreme by Newtonian fluids. The

deformation of a solid material may reverse spontaneously when the external forces are removed. A Newtonian fluid flows when a force is applied, but when the force is removed the flow ceases and is not reversed (Fig 2). Most materials, including those of a colloidal nature, exhibit non-Newtonian behaviour which is in between these extremes; such materials are said to be viscoelastic (Fig 3).

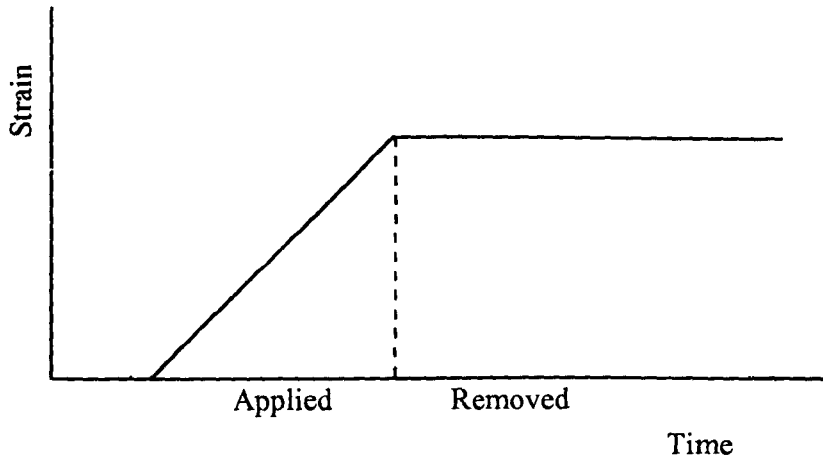


Fig 2 Newtonian fluid (viscous) behaviour

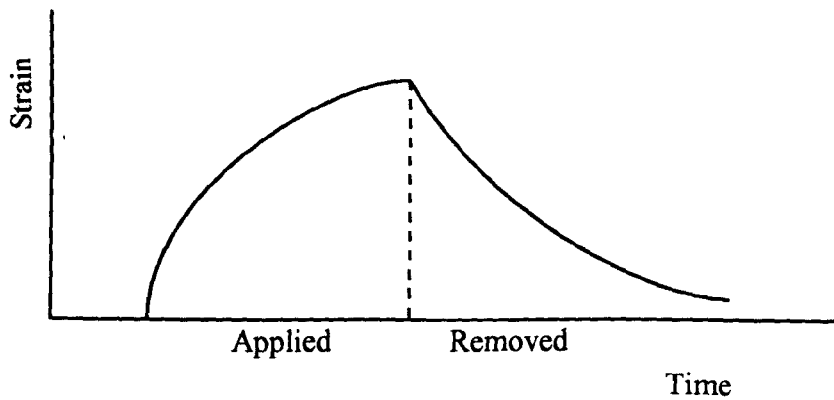


Fig 3 Viscoelastic behaviour

Viscoelastic materials are time-dependent i.e. the response to an applied force depends on the time-scale involved. A common example used to describe such behaviour is the response of 'funny putty' to varying applied forces. A ball of this material will bounce when dropped onto a hard surface, where its contact time is of the order of a few milliseconds. If the time-scale of the applied force is increased to seconds, e.g. by squeezing, the material will flow. This observable phenomenon depends on the ratio of the time it takes for the system to relax to the time taken to make the observation. This ratio is called the Deborah number De .

$$De = \text{relaxation time} / \text{observation time} \quad (4)$$

When De is very small, the system behaves like a fluid and conversely, when De is very large the system behaves like an elastic solid.

Flow involves the relative motion of adjacent elements of a material. The rheological behaviour of colloidal dispersions will depend on several factors such as the viscosity of the dispersion medium, particle concentration, particle size and shape, and interparticle forces. The combination of these factors will determine if a material is subject to Newtonian and/or non-Newtonian behaviour. The printing process involves more than one relaxation time

1.4.3 Viscosity

In order to appreciate Newtonian and non-Newtonian behaviour, the concept of viscosity must be understood. The viscosity of a liquid is a measure of the internal resistance offered to the relative motion of different parts of the liquid³. Consider the situation when a fluid is contained between two plates parallel to the xy -plane and a distance h apart along the z -axis (Fig 4).

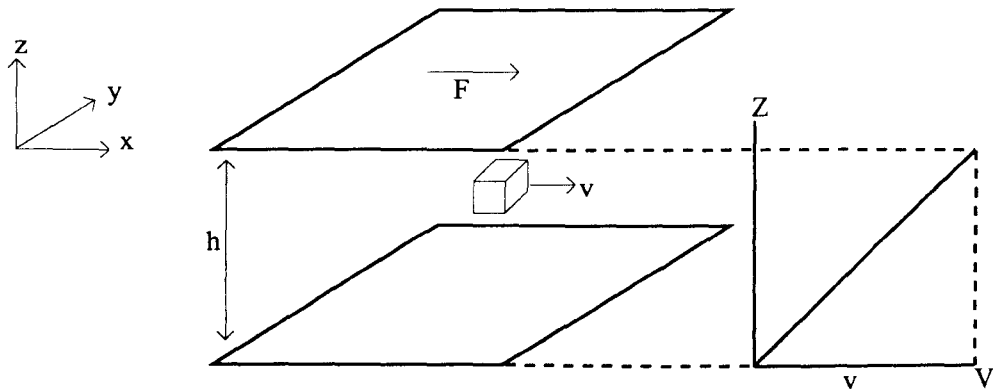


Fig 4 Representation of a simple shear field between two parallel plates

The plates are maintained in a relative motion at a constant velocity V in the x -direction by a shearing force F applied to the upper plate. The velocity of movement, v , of an element of fluid relative to the lower plate increases linearly from zero at $z = 0$ to V at $z = h$. The ratio V/h is called the shear rate $\dot{\gamma}$. The force needed to maintain the steady motion is proportional to the area of the upper plate, A , over which the force is applied, and the ratio F/A is called the shear stress τ . The ratio of $\tau/\dot{\gamma}$ is called the viscosity η .

1.4.4 Newtonian and non-Newtonian systems

A system may be described as Newtonian when the viscosity is constant and independent of shear rate (Fig 5a). Such behaviour is exhibited by simple molecular liquids and dilute colloidal systems^{3,4}.

In non-Newtonian systems the viscosity is dependent upon the shear rate, and also generally, on the history of the system^{3,4}. Some typical types of behaviour are given in Figs 5b-f. If the apparent viscosity of a material increases with the applied shear stress, it is said to be dilatant or shear thickening (Fig. 5b).

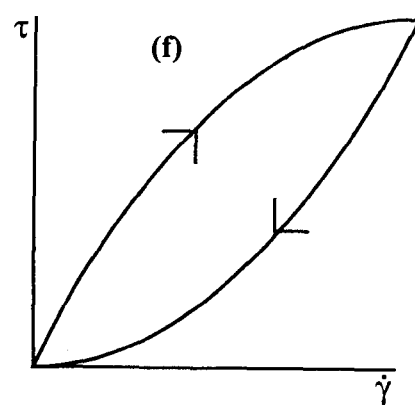
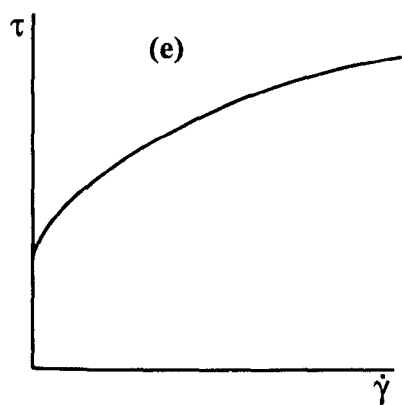
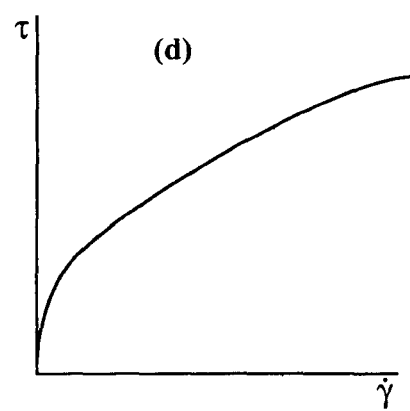
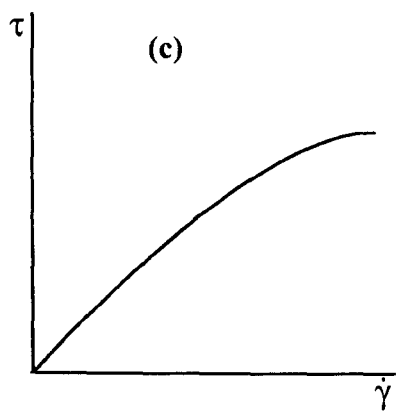
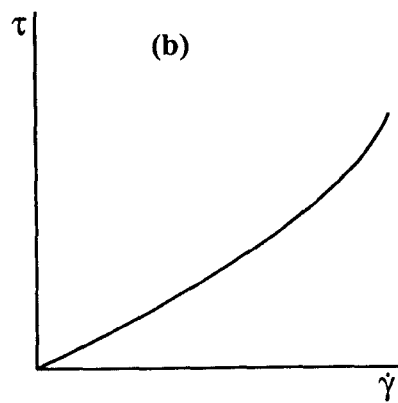
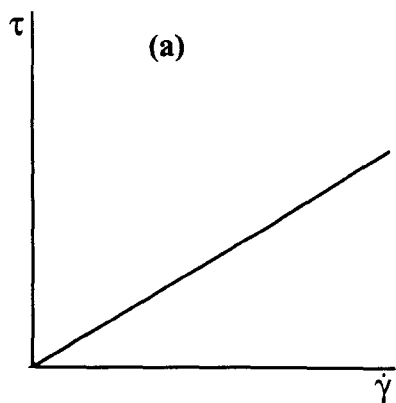


Fig 5 (a) Newtonian behaviour
 (b) Shear thickening
 (c) Shear thinning
 (d) Pseudoplastic
 (e) Plastic
 (f) Thixotropy

Conversely, if a decrease in apparent viscosity with increasing shear stress occurs, then a material is said to be shear thinning (Fig 5c). This behaviour is particularly common in systems containing asymmetric particles. Such particles disturb the flow lines to a greater extent when they are randomly orientated at low velocity gradients than when they have been aligned at high velocity gradients.

A more extreme case of shear thinning, called pseudoplastic behaviour, is shown in Fig 5d. In plastic systems (Fig 5e) there is no initial response to the applied stress. However, when a limiting yield stress (τ_0) is reached, the material begins to flow.

Some materials exhibit non-Newtonian behaviour which is time-dependent. This is particularly common in a colloidal system. If a shear stress is removed from a material after shear thinning and on standing the structure of the material is regained, it is said to be thixotropic (Fig 5f).

Printing inks generally display shear thinning or pseudoplastic behaviour as well as thixotropy¹³⁻¹⁷.

1.4.5 Rheology of suspensions of colloidal particles

The dispersion of colloidal particles in a liquid will alter its viscosity. The flow of the liquid is disturbed by the presence of colloidal particles and the resulting viscosity is higher than that of the pure liquid. The viscosity of such a dispersion is dependent upon the size, shape, and concentration of particles and also interparticle relationships⁴.

Einstein (1906)¹⁸ developed a theory relating the disturbance of flow lines when identical, non-interacting, rigid spherical particles at low concentrations are dispersed in a liquid medium. The relative viscosity, η/η_s where η_s is the viscosity of the pure liquid medium, is related to the volume fraction, ϕ , of particles by the equation

$$\eta/\eta_s = 1 + 2.5\phi \quad (5)$$

The effect of such particles on the viscosity of a dispersion therefore depends only on the total volume which they occupy and is independent of their size. The above equation may also be expressed in terms of the relative viscosity increment, η_i .

$$\eta_i = (\eta - \eta_s) / \eta_s = 2.5\phi \quad (6)$$

$$[\eta] = \eta_i / \phi = 2.5 \quad \phi \rightarrow \infty \quad (7)$$

where $[\eta]$ is referred to as the intrinsic viscosity.

For dispersions of non-rigid spheres (e.g. emulsions) the flow lines may be partially transmitted through the suspended particles, making the intrinsic viscosity less than 2.5.

Whereas the Einstein equation is valid for very dilute suspensions (i.e. where the mole fraction is less than 0.02), it is not valid at higher concentrations¹². This is due to an overlapping of the dispersed regions of flow around the particles. The influence of

neighbouring particles must therefore be considered. Thus equation (6) may be seen as the first term of an expansion.

$$\eta_i = 2.5\phi + 6.2\phi^2 + k_3\phi^3 + \dots \quad (8)$$

The shape and symmetry of a particle will affect the viscosity of the dispersion. An asymmetrical particle dispersed in the continuous phase will disturb the flow lines to a greater extent thus increasing the effect on viscosity.

If the dispersion contains charged particles, there will be increased resistance to flow. Extra energy will be required to overcome the interaction between ions in the double layers around the particles and the electrical charge on the particle surfaces, thus leading to an increased viscosity.

1.4.6 Ink formulation and rheology

In order to establish the criteria for formulating lithographic inks to the appropriate rheological properties, it is necessary to examine the demands placed on the inks as they pass through the high speed press.

Initially, the ink is placed in an ink duct where it maintains its high viscosity. The ink is metered out through the duct onto the first distribution roller. This occurs under conditions of relatively low shear and the ink begins to flow as a result of shear thinning. The ink is delivered to the printing plate via a long series of distribution rollers, then it is transferred to the blanket. The sequential splitting of the ink film eventually results in a film of 1-3 microns in thickness being delivered to the substrate.

The ink film is subjected to pressure variations (both positive and negative) as it is forced through each nip at speeds of 10-13 ms⁻¹ for a high speed press^{19,20}. The ink is subjected to high mechanical shear forces which it must be able to withstand. The flow

properties of the ink become more critical as the increasingly thinning films cover the distributing rollers.

In transferring the image from the plate, the ink must have a degree of thixotropy in order to maintain the integrity and sharpness of the image²¹. The thixotropic behaviour of the ink limits the dot spreading as the structure is regained on the substrate.

Finally, after the ink has been transferred to the substrate, it should dry to form a rub-resistant film.

It can be seen that the ink must be able to react to a range of different shear conditions; to reduce its viscosity in order to cover the roller surfaces, then regain its structure quickly when the stress is removed. Such behaviour is typical of viscoelastic materials.

1.5 Fountain solutions

The major roles of the fountain solution are to wet the non-image areas of the lithographic printing plate, desensitise them to printing inks and also to cool the plate^{2,22}. Water alone does not wet the surface of the plate effectively because of its high surface tension. Commercial fountain solutions tend to be a balance of various chemicals whose primary function is to improve the wetting characteristics of the water relative to the plate, thus keeping the non-image areas free of ink. Propan-2-ol, which is known in the printing trade as isopropyl alcohol (IPA), is used in conjunction with fountain solution; however, its role will be discussed later (section 2.7). Generally, fountain solutions consist mainly of water (98%) with the remaining components acting to enhance its interactions with the printing plate. The formulations of commercial fountain solutions are never disclosed, but the following generic groups of components may be present in fount concentrates.

Film-forming agents have several functions: the maintenance of a water receptive non-image area; the protection of the non-image areas during press stoppages as well as the

quick run up of inks when printing is resumed. Historically, gum arabic has been used for this purpose because it is highly water-soluble and forms a non-porous film over the non-image area. The film formed has a high affinity for the aluminium oxide on the surface of the non-image areas of the plate, thus rendering them extremely hydrophilic. The gum arabic will adhere to the non-image areas, but it is repelled by the image areas. The main disadvantage of gum arabic is that it is not compatible with IPA and so synthetic alternatives are now widely used.

Although film-forming agents may also act as desensitisers in that the non-image areas are kept ink free, additional desensitisers may also be included in the formulation. These chemicals react with the non-image areas to increase their hydrophilicity. Desensitisers are the main active components of fountain solutions and provide a continuous means of preventing scumming. This is necessary because gum arabic is eventually worn away by repeated contact between the roller and the blanket. Examples of desensitising compounds that are commonly used are fluorides, phosphates, nitrates and organic compounds such as phosphate esters.

A buffering system is required in order to maintain the pH of the fountain solution. Acidic or alkaline founts are used according to preference. It is common practice to use salts which can also act as desensitisers; hence, a citrate or a phosphate may be used.

Surfactants may be used in formulations where their principal role is to lower the surface tension of the fountain solution. This allows a thin film of fount to wet the surface of the plate rapidly and aid absorption of water into the ink. These properties are similar to those imparted by isopropyl alcohol. Generally, two types of surfactants are used; they are either anionic or block co-polymers.

Humectants such as glycols or polymeric surfactants are sometimes included in formulations. This group of compounds may be considered as being non-drying materials

which leave a thin wet film on the plate surface during press stoppages, therefore preventing the non-image areas from drying.

In formulating a fountain solution, the local water hardness of the printing environment needs to be established. The control of water hardness is considered by some authorities to be of paramount importance. It has been found that very hard water can cause problems with calcium deposits causing ink stripping on the blanket and the inking rollers. In order to optimise conditions, sequestering agents are added to the fountain solution.

Other chemicals are added to the fount concentrate which do not necessarily influence the action of the fountain solutions. Examples of these are biocides (which prevent bacterial growth in the dampening system), and corrosion inhibitors (which protect the metal parts of the press). Anti-foams may also be used to counteract the effects of surfactants.

It is clear from the above discussion that the additives included in fountain solution concentrates appear to interact with the surface of the printing plate and not necessarily with the lithographic ink. The experimental work detailed in this thesis is concerned with off-line investigations which do not involve interactions with the printing plate. Therefore, demineralised water has been used as the basic fountain solution and isopropyl alcohol has been added when required.

2. Background

2.1 Ink and water interactions on the press

MacPhee proposed two models to describe the phenomena occurring in the lithographic printing process²³. The first is concerned with conventional lithography and involves a 'plate-feed system' (where ink and water are fed to the plate via separate roller systems). The second model is concerned with an integrated 'ink-feed system', more specifically the Dahlgren dampening system (where water is fed to the plate via the inking system).

2.1.1 MacPhee's model for the plate feed system

In the plate-feed system the dampening rollers are either chrome plated or cloth covered so that they are preferentially wetted by conventional fountain solutions (i.e. without alcohol). When the dampening rollers and inking rollers apply fountain solution and ink sequentially to the printing plate the following events occur at the nips (Fig 6).

Firstly, when the dampening rollers pass the hydrophilic non-image areas, a single film of fountain solution is present in the nip (Fig 6a). At the nip exit, the film splits leaving a film of fountain solution on the plate.

Secondly, the fountain solution comes into contact with the lyophilic image areas which are usually covered with a residual ink film (Fig 6b). The two liquids are subjected to converging flow at the nip entrance and some of the fountain solution is emulsified into the ink due to shearing. At the nip exit, there is a composite film (consisting of a water layer and an ink layer), in which splitting occurs within the low viscosity water layer, leaving water globules on the surface of the ink which are referred to as 'surface water'. This surface water is formed as a result of the high contact angle of the fountain solution relative to the ink.

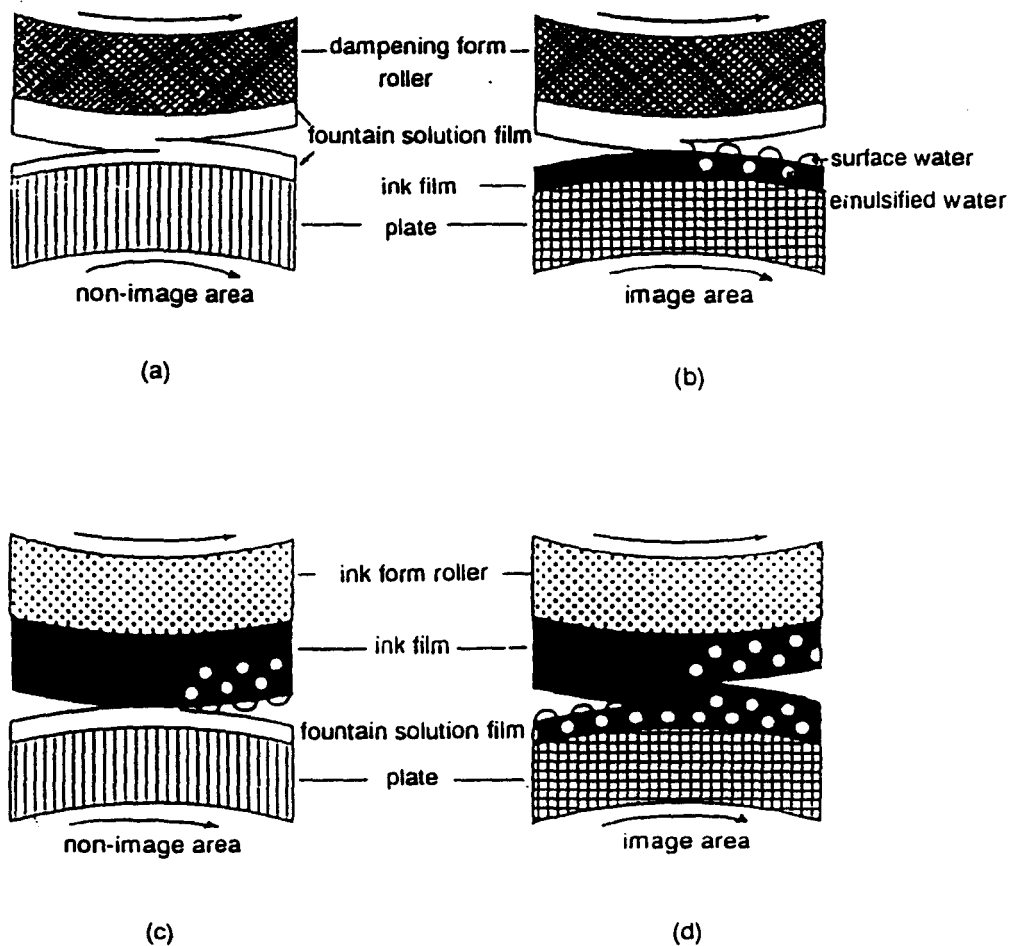


Fig 6 Shows the processes occurring in the nip region for the image and non-image areas

Thirdly, the dampened non-image areas pass the inking rollers (Fig 6c). A composite film containing a water layer from the plate and an ink layer from the roller is present in the nip. At the nip entrance, the fountain solution is emulsified into the ink film. At the nip exit, the splitting of the composite film occurs within the weakest layer leaving a residual film of water on the plate. The remaining water is transferred back through the inking train.

Finally, the dampened image area passes the inking rollers (Fig 6d). The inked image area has small droplets of fountain solution on the surface which are pressed against the inked forme roller. These droplets of fountain solution become emulsified into the ink, thus producing a single film of ink containing dispersed droplets of fountain solution. At the nip exit, the ink film splits and deposits the emulsified ink film on the image area.

2.1.2 MacPhee's model for the Dahlgren system

In the second model (Fig 7) MacPhee pointed out that the ink-feed system required alcohol to be used with the fountain solution²³. The presence of alcohol results in a decrease in surface tension to 29 mNm^{-1} compared with a reported value of 54 mNm^{-1} for a conventional fountain solution. The reduction in the surface tension of the fountain solution improves its ability to wet the surface of an inked surface, thus ensuring sufficient transport of fountain solution to the plate.

Initially, the dampening roller deposits a film of water on the surface of the ink forme roller (Fig 7a). When this contacts the non-image area the composite film splits in the water layer, thus leaving a film of fountain solution on the plate and a residual film of surface water on the ink forme roller. At the entrance of the nip between the forme roller and the vibrating inking roller, the shear conditions result in the emulsification of the surface water into the ink.

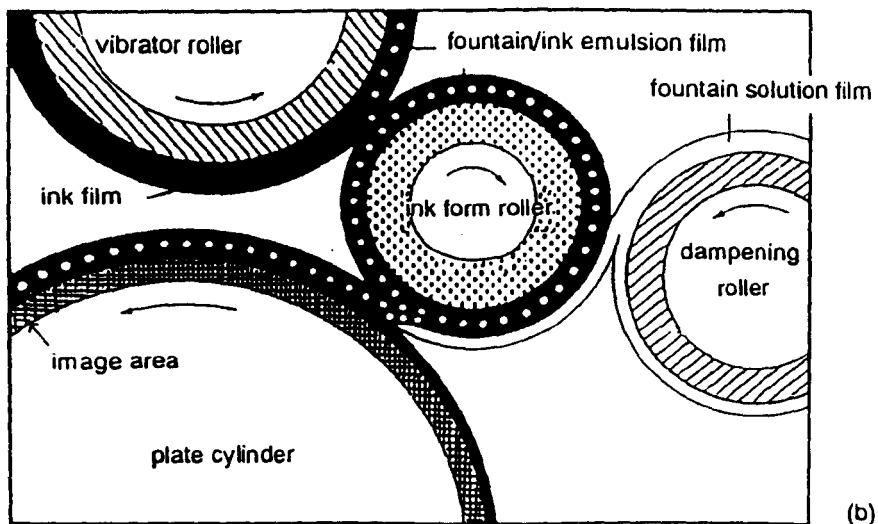
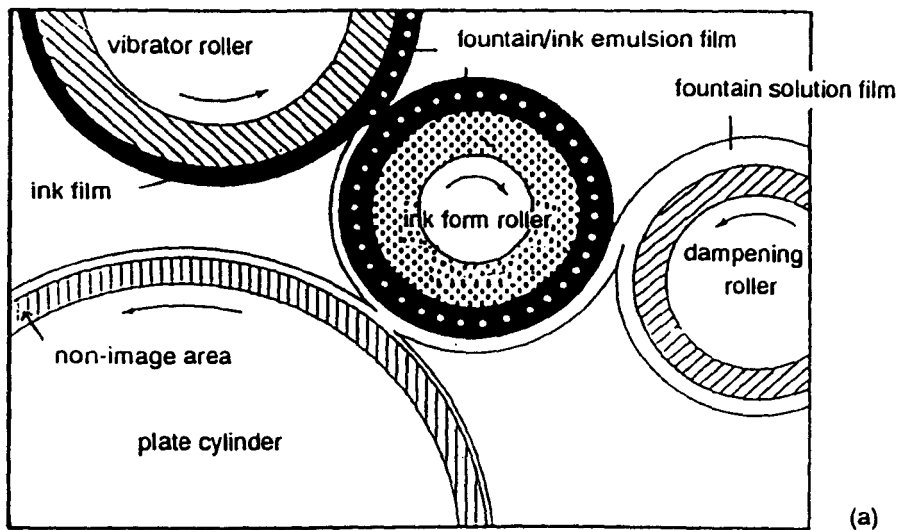


Fig 7 Shows emulsified and surface water at the nip regions in the ink feed dampening system.

At the entrance of the nip between the image area and the dampened ink forme roller, the fountain solution on the surface is emulsified into the ink, thus forming an emulsified ink film (Fig 7b). At the nip exit the emulsified ink film splits and further emulsification takes place when the ink forme roller meets the vibrating ink forme roller.

It is clear that this system results in a greater amount of fountain solution being emulsified into the ink in comparison with a plate-feed type system. It has also been reported that the extent of emulsification is greater in an ink-feed system than for a plate-feed system²³.

2.1.3 Ink/water balance

The above models assume that the ink film thickness on a plate is 2-3 microns, whereas the thickness of the fountain solution film is 0.5-1 micron. This ratio of ink film thickness to fountain solution thickness is often referred to as the 'proper ink-water balance'²³. The value of this ratio depends on the nature of the press and the particular ink and fountain solution used.

If the fountain solution fed to the plate is increased above this level, then over-emulsification is likely to occur causing the final printed image to have a washed-out appearance. Phase inversion may also occur resulting in tinting, where ink is emulsified into the fountain solution and deposited onto the non-image areas.

Conversely, if the fountain solution feed is reduced below the 'proper' level, the film of fountain solution on the non-image areas will not be of sufficient thickness to keep these free of ink²³. This will result in a phenomenon known as 'scumming', where ink residues are deposited onto the non-image areas of the plate.

The concept of ink/water balance can be modified to consider not only the limits for suitable ratios (of ink to water), but to include the tolerance of inks to changing levels of

fountain solution. At the optimum ink/water balance (i.e. after emulsification) the ink must not be 'sensitive' to the presence of fountain solution²⁴. An ink is said to be sensitive or less tolerant to the presence of water if fluctuations in the amount of fountain solution exceed these limits and consequently affect the print or flow properties of the ink. Therefore, in general, an ink which has a broad tolerance to water is said to have good ink/water balance. Conversely, an ink that is sensitive to water is said to have poor ink/water balance.

There are several factors which may affect the ink/water balance on a press. Under high shear conditions in the nip, emulsification and emulsion breakdown can occur, thus altering the amount of bulk water present; this can lead to roller stripping²³.

During press operation the input of mechanical energy via the roller system results in the generation of heat. Some of this heat will be dissipated by the cooling effect of water in the nips whereas the rest will remain in the emulsion. It is well known that an increase in temperature can promote emulsion breakdown. Therefore, in order to maintain the ink/water balance it is necessary that the emulsion should have some degree of thermal stability. An increase in temperature of approximately 15-25°C is considered to reduce the stability of many ink/fountain solution emulsions²⁵.

If any of the above changes occur, the water-feed and ink-feed to the printing plate will need to be adjusted accordingly. It also follows that the ink/water balance is a function of press operating conditions; this has implications for the formulations of ink and fountain solutions for differing press conditions.

2.2 Press emulsification tests

The lithographic printing press provides the ultimate method of determining the runnability and printability of an ink and fountain solution. On a single press run it will become apparent if the surface and rheological properties of the ink and fountain solution

are inadequate. While a press trial gives a qualitative assessment of the emulsification properties of an ink, it would probably be more useful as a diagnostic tool if it also provided quantitative information.

It is not possible to correlate findings from one press trial with another unless it is held under identical printing conditions (e.g. temperature, ink film thickness, image area, press speed and water feed level)²⁶. MacPhee examined inks tested under standard conditions where the ink film thickness was 2-3 microns on the image area and the thickness of the fountain solution film on the non-image areas was 0.5-1.0 microns. It was found that the emulsion capacity of the inks studied was in the range of 15-30% with a measured water content of 23%. Douw and Blokker found similar emulsification capacities in the range of 10-33% for two heatset inks; however, the conditions were not specified²⁷.

Several attempts have been made to determine the amount of emulsified water present in an ink. In a study of news inks, Lindqvist found that an emulsion removed from the ink forme roller closest to the water fountain contained 24-34% water²⁸. However, it was also found that when a sample of the emulsion was removed from the roller furthest away from the water fountain it contained 12-15% water. This difference may have been caused by the loss of water through evaporation, which underlines the importance of temperature control. In any case, it could be argued that the location from which an emulsion sample is removed must be specified in order to make useful comparisons.

Cunningham and Moore studied sheet-fed offset inks on a press and reported a range of water contents for each of the inks sampled²⁹. A magenta ink was found to give varying water content between 4 and 22% when samples were removed from the fountain forme roller. It is possible that the discrepancy between these results may have arisen because of the size of the samples tested. Samples of between 50 and 70 mg were removed from the moving press and the water was measured using the Karl-Fischer Titration method. Such small samples would mean that any sample to sample variations, for example those caused by evaporation, would be greatly amplified and are therefore more critical.

The method of sampling and its contribution to the water content measurements have also been questioned. Tasker et al stated that the method of sampling was itself an emulsification process leading to high and erratic values of water content³⁰.

2.3 Off-line emulsification tests

In addition to the problems of evaluating the emulsification properties of inks on a printing press outlined above, the process is expensive in terms of material, energy and efficiency. In order to address this problem many off-line methods have been put forward to examine the emulsification characteristics of lithographic inks so that their subsequent performance on the press can be predicted.

To this aim, a number of laboratory devices have been developed. Results have been reported using mixers and various shear regimes i.e. the Duke Tester^{29,31} and the Sunbeam Mixmaster^{32,33}. Laboratory roller systems, such as the Lithobreak Tester³⁴ and the Lithomat Tester³⁵, have been used as model press systems.

A number of the emulsification investigations were based upon establishing how much fountain solution is absorbed by an ink over a given period of time. Traditionally, the amount of fountain solution absorbed has been measured gravimetrically or by use of the Karl-Fischer Titration method²⁹.

The classic quantitative emulsification test proposed by Surland has been widely reported^{32,33,36}. The Surland emulsification test was based on the assumption that most inks achieve equilibrium within 10 minutes of the introduction of water. The test involved mixing fresh ink (50g) with fountain solution (50 cm³) for 1 minute at approximately 90 rpm in the Sunbeam Mixmaster. After 1 minute, the stirring is stopped and any excess fountain solution decanted. The amount of fountain solution in the ink is determined gravimetrically. This procedure is repeated successively until a total mixing time of 10 minutes has elapsed.

The situation on the press can be described as one in which emulsion formation and emulsion breakdown occur, but not necessarily at the same rate.

Surland developed this theory further by relating the rate of emulsification to the feed rates of water and ink on the press. The following expression was proposed³³:

$$\begin{array}{ccc}
 W + O & \xrightleftharpoons{\hspace{1.5cm}} & W/O \\
 & \downarrow & \\
 & P = P_+/P_- &
 \end{array} \quad (9)$$

where W is the water feed, O is the ink feed, and the arrows can be considered as 'vectors' respectively for emulsion formation (P_+) and emulsion breakdown (P_-).

On the press P_+ must initially be greater than P_- in order to achieve the emulsion capacity of the ink. A steady equilibrium will therefore be achieved on the press when P_+ and P_- become equal, (i.e. when $P = P_+/P_- = 1$).

In examining the rate of water uptake of several inks, Surland found that inks could be classified by five characteristic curves, i.e. PA, PB, PC, PD, PE, which are collectively known as P curves (Fig 8). This could be extended further to state that the behaviour of the ink on a press will depend upon how it interacts with a specific fountain solution.

These curves may be interpreted as a set of possible conditions where the y-axis (percentage emulsification) represents one limit, of full mixing between the ink phase and the fountain solution phase; the x-axis represents the other limit, of absolute repulsion between the two phases.

At either extreme of the diagram it can be seen that curves PA and PE are almost linear functions indicating poor press performance. Inks of these types are unable to attain any

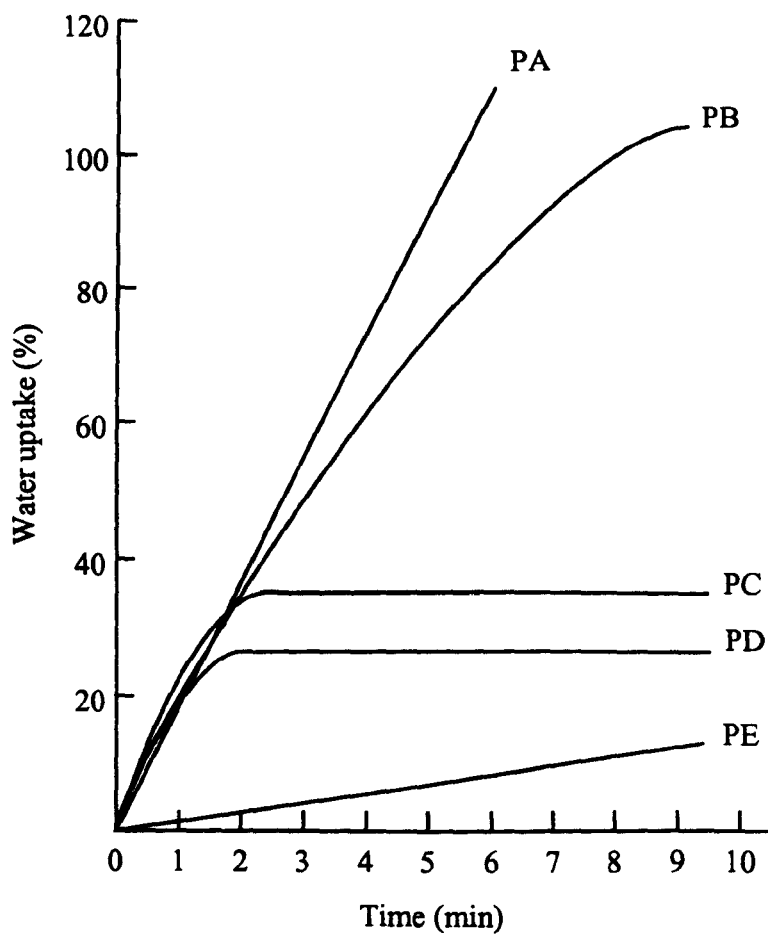


Fig 8 Typical emulsification curves (P-curves) according to Surland

kind of equilibrium or water balance on the press. This means that prints of an acceptable quality cannot be produced on the press.

An ink with a PA type curve absorbs water too rapidly. Initially, a fountain solution/ink emulsion is formed. However, the volume of water absorbed by this ink would eventually lead to phase inversion where an ink/fountain solution emulsion is formed. This would result in the ink being carried into the water-feed system where it will be deposited on the non-image areas of the plate, thus causing tinting. The printed image would also have a washed-out appearance because of the presence of large quantities of water in the emulsion.

An ink with a PE type curve appears to be almost totally immiscible with water. In this case, a heavy film of water which has been picked up from the non-image areas of the plate in the plate/ink forme nips would lay across the surface of the ink forme thus causing image blinding i.e. a situation where no image at all is produced.

A PB type ink absorbs water rapidly initially; however, the rate of water uptake slows down but does not reach equilibrium. This ink absorbs a large amount of water and would appear to be partially miscible in water. Such an ink is said to have a narrow water balance; thus the ink and fountain solution feed rates would need to be re-adjusted frequently to maintain adequate print quality. PB type inks would be prone to producing mottled solids, scumming and dot spread/gain. This illustrates the relationship between feed rates and ink/water interactions with regard to the required outcome of the process. This emphasises the need for an understanding of the concept of ink/water balance.

A printed lithographic image is formed from many dots of varying sizes which enhance the image by giving improved definition. Dot gain can be a function of the viscosity of the ink (emulsion); i.e. the presence of water will lower the viscosity of the ink causing the dot to spread and increase in size. Therefore, if a large amount of water is absorbed

by the ink (e.g. in a type PB ink), then an increase in dot size is expected, thus giving rise to a loss of image definition or sharpness.

Mottle may be described as uneven print density which will be seen in areas of solid print. If a non-uniform emulsion is formed, which may occur if too much or too little water is absorbed by the ink, then this may produce mottle¹.

The PC type ink absorbs water rapidly during the first 2-3 minutes of testing, but thereafter the amount of water taken up appears to be constant. Such an ink should be able to reach a steady state equilibrium on the press where the rate of emulsion formation and the rate of emulsion breakdown are equal. Therefore only minor adjustment of the ink and water feed will be required. The behaviour of this type of ink was described as 'ideal', where the level of water emulsified does not interfere with print quality, i.e. the solid areas print with even density and the plate image is reproduced with high fidelity.

The PD type ink initially absorbs water at a slower rate in comparison to the PC type ink. This ink also reaches a constant level of water uptake. However, it is clear that a PD ink absorbs less water than a PC ink, which indicates that the ink and fountain solution do not mix well. Such an ink would have a narrow water balance and would tend to give dot sharpening, mottled solids and low print density.

The Surland emulsification test has been well established within the ink and printing industries as a predictive test for the suitability of ink and fountain solution pairs^{32,33,36}. However, despite the extensive use of this method, it is known that some ink and fountain solution pairs that have produced 'ideal' Surland emulsification curves have been found to give unacceptable print quality and vice versa. Such observations lead to the conclusion that while the rate of water uptake is of significance, there may be other aspects of the emulsification process which affect print quality.

The Surland test is a measure of emulsification rate and capacity, i.e. the extent to which the fountain solution, as the disperse phase can be emulsified under specified conditions. It is possible that the discrepancies in the predicted behaviour of an ink and fountain solution on the press by the Surland method may be explained by examining not only the mechanisms of emulsification but also the nature of the emulsions formed. However, this particular method gives no information about droplet size, droplet size distribution and rheological changes that may occur. Bassemir and Shubert postulated that a combination of emulsification tests and rheological studies would give more accurate predictions of press performance³⁷.

While undoubtedly useful, the Surland test cannot stand alone as the definitive laboratory test method for predicting ink performance as it yields only part of the information necessary for the assessment of press performance.

2.4 Effects of shear conditions on emulsification

The fact that the Surland emulsification test is performed under relatively low shear rate conditions in comparison to press tests has been cited as a major reason for the lack of correlation of ink behaviour between the two procedures. Chou et al noted that differences in shear rates in off-line systems resulted in the formation of emulsions of a different quality and uniformity³⁸.

This problem has been addressed through the work of Thormählen³⁹. The Litho-lab roller system was developed to examine the major elements of ink/water interactions while adopting similar shear regimes to that of a sheet-fed printing press. This device was used to measure the amount of water on the non-image area, the water and ink content on the image areas, ink film thickness and wet tack. A running speed of 6.6 ms^{-1} was used and a temperature control device was incorporated. It is well known that viscosity, printability and water content are strongly dependent upon temperature. Therefore it is necessary to control temperature effects in order to achieve constant results. Similar

parameters were measured on a sheet-fed lithographic press. It was found that under the above conditions the Litho-lab gave results comparable with those from the press.

The above examples highlight the need to conduct off-line emulsification tests under suitable, well-defined shear regimes in order to give meaningful results.

Chou and Cher compared the stability of fountain solution/ink emulsions under low shear rates (i.e. $0-100 \text{ s}^{-1}$) and higher shear rates (i.e. $100-300 \text{ s}^{-1}$), with that of the corresponding fresh ink⁴⁰. In examining the thixotropic flow curves under these conditions it was found that the emulsion became less stable at the higher shear rates whereas the rheological behaviour of the fresh ink remained stable under shear. The instability of the fountain solution/ink emulsion was thought to occur as a result of the deformation and coalescence of water droplets.

It was proposed that when shear stress is applied to the emulsion, the spherical water droplets are deformed into 'prolate' spheroids. The applied stress affects the stability of the emulsion in two ways. Firstly, the surface to volume ratio of the water droplet is increased, thus causing a reduction in the stability of the interfacial region. Secondly, the collision radius of the dispersed droplets is increased. These factors result in an increase in the rate of coalescence of the water droplets and therefore governs the shear stability of the fountain solution/ink emulsions.

At low shear rates, the shear forces do not provide enough mechanical energy to cause the necessary level of deformation to encourage the above effects. Under such conditions, the rheological behaviour of the fountain solution/ink emulsions is said to be similar to that of a homogeneous fluid instead of a two-phase system.

However, as the shear stress is increased, the shear forces can now provide sufficient mechanical energy to overcome the interfacial forces. The dispersed water droplets become significantly deformed thus increasing the possibility of coalescence into larger

droplets or discrete layers of water. Under such conditions, the rheological behaviour is typical of a heterogeneous mixture. In this form, the water may evaporate or become broken down into smaller droplets which are re-distributed within the ink.

In addition to the above, the shear stability of a fountain solution/ink emulsion was found to be affected by the amount of fountain solution absorbed by the ink. The shear stability of the emulsion was found to decrease with increasing water content under high shear conditions.

The above observations⁴⁰ raise the question of how stable should an emulsion be to perform well on a press? It has been found that if the emulsion is too stable then the flow and transfer of the ink will be retarded. However, if the emulsion is too unstable it could cause image blinding or tinting.

2.5 Memory effects of printing inks

During the printing process the ink undergoes high shear stress at the roller nips but relatively little shearing between two successive passes through the nip. Lithographic inks are applied through a long series of rollers before meeting the nip at the printing plate.

The rheological effects of successive shearing were investigated by Pangalos et al ¹⁹. The transient response of typical lithographic inks was measured under pulsed and bidirectional shear, where the direction of the applied shear is changed during the experiment.

In the first experiment the shear rate was raised from zero to a preset value then the shear stress was allowed to reach equilibrium. Shearing was discontinued for varying amounts of time and then restarted with the same magnitude of shear. It was found that when shearing recommenced the ink exhibited a stress decay or thixotropic response to the repeated shear rate step changes. However, if a longer 'rest period' was allowed between

shearing then this would result in a greater stress peak height at the start of the next period of shearing.

In the second experiment the direction of shear was reversed suddenly. Under these conditions the stress curve resembled that of an elastic liquid response. Further to this, it was found that decreasing the speed in one direction, increased the speed with which the stress reached equilibrium in the opposite direction. Clearly there are memory effects relating to transitory orientation effects or internal entropy changes influencing the emulsification process.

Whereas the bidirectional shear experiments described here may not be of direct significance to the lithographic process, the stepwise shearing of the first experiment has implications to the mechanisms taking place when the press is restarted after stoppages. The magnitude of the time elapsed during the 'rest periods' and also the maximum length of time that these memory effects remain active were not made clear; however, it can be estimated that such effects would be short lived i.e. of the order of a few minutes.

2.6 Role of surface water

The emulsification rate and capacity of inks is the main concern of Surland's work. The equilibrium expression (equation 9) implies that emulsion break-down or demulsification is a necessary part of the process, but its relevance is not clarified by Surland.

Fetsko²⁶ and also Rosenberg⁴¹ pointed out that the lithographic process not only requires a stable fountain solution/ink emulsion but also that the emulsion should become less stable under the shear conditions at the roller nips. This results in water release or the production of surface water. The function of surface water is to protect the non-image areas of the plate by wetting and removing any ink deposits which would otherwise cause scumming²³.

In an attempt to clarify the role of surface water in lithography, Rosenberg made a distinction between emulsified water and surface water. Sufficient ink was applied to a roller system to give an ink film thickness of 10 microns. Fountain solution (deionised water) was applied to the rollers by a spraying method. The determination of the amount of emulsified water was carried out when the spraying was stopped. The surface water was allowed to evaporate and then the emulsified water was measured. The difference between the water content during continuous spraying and that after spraying had stopped, yielded the relative amounts of surface water to emulsified water.

It was found that for an ink with a total water content of 15%, the emulsified water appeared as fine droplets approximately one micron in diameter. It should be noted that droplets of sub-micron diameters may also exist but cannot be optically detected. The surface water was distributed on the ink film with a range of droplet sizes of 10-50 microns. However, it was suggested that in order for water droplets to function as surface water they should be above 50 microns in diameter.

Whereas the emulsification of fountain solution is necessary, the production of surface water is more important in the lithographic process. This has similarities with an 'ideal' Surland curve, particularly in the latter region when an equilibrium is maintained over the last 5-6 minutes of testing; during this period, demulsification - which is necessary for the formation of surface water - occurs at a similar rate to droplet breakdown. This study implies that once the water droplets are emulsified, i.e. below one micron, they play no further role in the lithographic process.

Iwaki et al⁴², used image analysis to determine the amounts of emulsified water and surface water. It was found that surface water appears when the droplet size diameter is in the range of 0.3-100 microns. This together with Rosenberg's observations raises the question of emulsion stability. It is likely that when droplets less than one micron in diameter are dispersed, they will be colloidally stable and therefore less likely to coalesce. At the other extreme, water droplets above 50 microns in diameter can function as surface

water, evaporate, or become broken down into smaller droplets. It is possible that the intermediate droplets which would lie mainly within the range of 1-50 microns can either become irreversibly emulsified or the droplets may coalesce. The three 'groups' of water droplets contribute to the overall metastable state of the emulsion. The formation of such an emulsion enables the non-image areas of the plate to be cleaned as a result of the production of surface water from emulsified droplets.

The amount of surface water formed and the size of the droplets is dependent upon the nature of the inks and fountain solutions together with the shearing conditions. A fountain solution with a high surface tension yields a greater amount of surface water; conversely, a fountain solution with a low surface tension produces a greater amount of emulsified water⁴³. This illustrates the need to optimise the interfacial properties of the fountain solution with the ink.

2.7 Role of isopropyl alcohol in lithography

Isopropyl alcohol (IPA) has been a long established additive to fountain solutions in lithographic printing. When approximately 20% by volume of IPA is added to the fountain solution, it is claimed that there is a more rapid attainment of water balance, less water is transferred to the printing plate and subsequently to the paper. Further to this, it is also claimed that the volatility of IPA is such that it facilitates the rapid evaporation of the fountain solution on the press⁴⁴.

Karttunen et al⁴⁵ stated that 'to provide a feasible emulsion' the surface tension of the fountain solution must be low. This statement implies that a primary function of IPA is to lower the surface tension in order to facilitate the emulsification of the fountain solution into the ink. Conversely, it has been suggested that the activities of IPA are limited to the non-image areas of the plate and the dampening rollers²³.

It is therefore desirable to establish the role of IPA in the lithographic process.

The effects of IPA on the surface tension of fountain solutions are well known. Banks et al⁴³ showed that it was necessary to reduce the surface tension of the fountain solution to prevent scumming. This was explained, using the term oil to imply ink, in terms of the 'spreading pressure' π , which is determined by the difference between the surface tension of the fountain solution (γ_{water}) and the surface tension of the oil (γ_{oil}).

$$\pi = \gamma_{\text{water}} - \gamma_{\text{oil}} \quad (10)$$

If the surface tension of the oil is less than or equal to the surface tension of the water, the oil will spread on the surface of the water.

The above may be expressed in terms of the spreading tension σ , between two immiscible liquids. This involves the consideration of the work of adhesion (W_a^{ow}) at the oil/water interface and the work of cohesion (W_c^{ov}) at the oil/vapour surface.

The work of adhesion for an oil/water interface is given by the Dupré equation:

$$W_a^{\text{ow}} = \gamma_{\text{wv}} - \gamma_{\text{ow}} + \gamma_{\text{ov}} \quad (11)$$

where

γ_{wv} = surface tension at the water/vapour interface

γ_{ow} = surface tension at the oil/water interface

γ_{ov} = surface tension at the oil/vapour interface

The work of cohesion which needs to be overcome in order to pull two surfaces apart thereby creating two oil/vapour interfaces may be expressed as:

$$W_c^{\text{o}} = 2\gamma_{\text{ov}} \quad (12)$$

Spreading will occur when $W_a > W_c$. It therefore follows that the 'spreading tension' σ is:

$$\sigma = W_a^{ow} - W_c^o \quad (13)$$

$$\sigma = \gamma_{wv} - \gamma_{ow} - \gamma_{ov} \quad (14)$$

In this case spreading will occur when σ is positive.

In order to overcome scumming it is necessary to reduce the surface tension of the fountain solution to a level approaching that of the surface tension of an ink⁴³ i.e. approximately 37 mNm⁻¹.

It is well known that the hydrophilicity of the non-image area of the plate promotes the complete wetting of these surfaces by the fountain solution. However, as stated earlier, the surface tension of the fountain solution is considerably reduced by the addition of IPA. It has been suggested that the reduced surface tension allows the fountain solution to wet the plate at a more rapid rate with a thinner film. Banks argued that 'in view of the fact that under normal conditions, i.e. with a properly desensitised plate, finite contact angles do not exist between the plate and the surface', it would be difficult to understand how surface tension would affect the film thickness⁴⁶.

It has been suggested that a major function of IPA is its interaction with the ink. Fadner, proposed that the main purpose of IPA is to enhance the transport of water to the plate by means of an inked roller⁴⁷. This occurs as a function of the reduced surface tension.

However, Douw and Blokker stated that IPA 'softened' ink by breaking down its structure resulting in a reduction in the viscosity of the ink²⁷. It was found that the addition of 1% IPA resulted in a 50% decrease in the viscosity of the ink. The 'softening' of the ink is said to promote the effective dispersion of fountain solution in the ink thus facilitating water uptake. Braun reported that the emulsion reached equilibrium at a faster rate when

15% IPA solution was included in the fountain solution³⁴. This was because IPA promoted homogeneous droplet size distribution with numerous finer droplets being formed. However, Iwaki et al, found that fountain solutions containing approximately 8% IPA gave a very broad size distribution of droplets throughout the emulsion⁴². This was found to give acceptable print quality. This aspect is re-examined in section 6. In addition to the above effects, the volatility of IPA causes the rapid evaporation of the fountain solution to occur, therefore less fountain solution is transferred onto the blanket which then reduces the amount of water entering the paper.

IPA was compared to surfactants of lower volatility and others which had a similar volatility to IPA⁴⁴. It was found that the surfactants tested, regardless of their volatility, could not be used in sufficient volumes to affect the rate of evaporation of the fountain solution, as is the case for IPA. These results could indicate that the volatility of IPA is such that it does not remain in contact with the ink for a long enough period to allow the IPA to act as a surfactant.

Mechanical energy is needed to move from the metastable to the stable condition. This is available to the printer who scrubs his plate with a rag soaked in a suitable solution, or in a press situation where this is input by shear in the nip (as in the MacPhee model). In order to reproduce these circumstances a modified Surland emulsification test is to be applied. An examination of Surland's conditions shows that the shear rates are not comparable to press conditions, with the result that there are differences in the droplet size distribution of the fountain solution/ink emulsions produced by these two methods. Therefore dispersion conditions with comparable shear rates are to be sought.

II METHODS

3. Experimental: Materials and equipment

3.1 Model varnish and ink systems

Model varnish and ink systems were designed in conjunction with DSM Resins for the purposes of this study. The criteria for the design of the ink vehicle were: standard polymer/rosin ingredients plus a variable ingredient whose hydrophilic nature can be selected within a range. It is therefore possible to formulate ink varnishes (without pigment) and the corresponding inks in which the water uptake properties range from 'hydrophobic' to 'hydrophilic'.

Each varnish formulation has the same basic ingredients: i.e. rosin modified phenolic resins, wetting alkyd resins, anti-oxidants and distillate. The variable ingredient comprises a modified hydrocarbon resin with enhanced water uptake, coupled with a lower molecular weight rosin modified resin to provide the appropriate solubility properties.

Initially, two varnishes of varying degrees of hydrophobicity were obtained from DSM; and later batches of the more hydrophilic varnish were prepared according to section 3.2. The label HL is used to represent the less hydrophobic (or more hydrophilic) varnish whereas the label HB is used to represent the more hydrophobic varnish. An additional varnish, LTHS, was also designed which was said to be a 'typical' formulation for a commercial lithographic heat-set varnish. All of these varnishes were formulated with a view that they should be suitable to run on a sheet-fed lithographic press. The formulations of the varnishes are given in Tables 2, 3 and 4.

Components	Parts dry
Haltermann PKWF 6/9 & PKWF 6/9 AFN (1:1 mixture)	395
Alsynol RL 54	140
Alsynol RL 43	150
Sheboffset 68147	190
Ionol CP (10% in mineral oil mixture)	10
Manalox 30A (20% in mineral oil mixture)	50
Alsynol PN 68	65
Total	1000

Table 2. Formulation of the model hydrophilic varnish

Components	Parts dry
Haltermann PKWF 6/9 & PKWF 6/9 AFN (1:1 mixture)	380
Alsynol RL 54	220
Necirez LX 685/150	290
Ionol CP (10% in mineral oil mixture)	10
Manalox 30A (20% in mineral oil mixture)	35
Alsynol PN 68	65
Total	1000

Table 3. Formulation of the model hydrophobic varnish

Components	Parts dry
Haltermann PKWF 6/9 & PKWF 6/9 AFN (1:1 mixture)	340
Sheboffset 68146	230
Alsynol RL 56	230
Manalox 30A (20% in mineral oil mixture)	35
Alsynol PN 68	70
PKWF 6/9 & PKWF 6/9 /AFN (1:1 mixture)	75
Total	980

Table 4. Formulation of the model LTHS varnish

The corresponding model inks were prepared by combining the varnish with a pigment paste. In this case a pigment paste containing cyan lutentia (a phthalocyanine blue pigment) supplied by DSM was used. The pigment paste consists of 35% solid pigment (by weight) which had been dispersed within a varnish base that is compatible with the model varnish systems. The pigment paste was incorporated into the varnishes so that the amount of pigment present in the resulting ink was 18% of the total weight.

The model varnish and ink systems described have several advantages over commercial systems. The proprietary nature of commercial inks, about which very little information is available, places constraints on any conclusions that may be inferred from studies of this nature.

While the model systems are comparable with commercial inks, they have two main advantages for this study. Firstly, a given varnish and ink specification enables experimental work to be carried out with a well-characterised system. Secondly, the separation of varnish from the pigment imparts a certain amount of transparency to the system which provides the opportunity for optical studies. In addition, examination of an

ink and its corresponding varnish will aid the study of the role of both the pigment and the varnish in the emulsification process.

3.2 Preparation of the hydrophilic varnish

A reaction vessel (1L) was placed in a heating mantle, in a fume cupboard. A petroleum distillate, PKWF 6/9 (170 g) and an anti-oxidant, Ionol CP (10 g of a 10% solution in PKWF 6/9) were added to the reaction vessel. The vessel was covered with a five-inlet lid in which a condenser, mechanical stirrer paddle, and a gas-inlet pipe connected to a supply of nitrogen were placed. A thermometer was also placed in the vessel so that the bulb was below the surface of the solvent. The final inlet was stoppered so that it could be used as an addition inlet.

The contents of the vessel were stirred together under nitrogen gas while being heated to 120°C. While the temperature was still rising, a phenolically modified ester, Alsynol RL 54 (70 g) was added over a ten minute period until it had dissolved to give an amber coloured solution.

An alkyd resin, Alsynol RL 43 (75 g) was then added to the solution over the next ten minute period.

When the temperature had risen to 180°C, a phenolically modified hydrocarbon resin, Sheboffset 68147 (95 g) was added over ten minutes while maintaining the temperature at 180°C.

When the Sheboffset had completely dissolved, the contents of the reaction vessel were cooled to 120°C. A gelling agent, Manalox 30A (25 g) (20% in PKWF 6/9) was added dropwise with continued stirring over ten minutes. The contents of the reaction vessel were re-heated to 150°C and kept at this temperature for 80 minutes to allow gelling to take place.

After this time the heat source was removed and an alkyd resin (containing linseed oil), Alsynol PN 68 (32.5 g) was added to the contents of the flask. After five minutes, a small sample of varnish was removed, drawn down a glass slide and examined for clarity.

When the varnish had cooled to 100°C, the remainder of the PKWF 6/9 (22.5 g)* was added to the varnish.

When the varnish had cooled to 50°C, it was filtered through a muslin cloth into a metal can and then left to cool overnight.

* It should be noted that the formulation used here differs from the hydrophilic varnish supplied by DSM in that only PKWF 6/9 is used. This is due to a variation in the solubility of one of the supplied resins.

3.3 Preparation of pigmented inks

Pigment paste (51.4 g) and the hydrophilic varnish (48.6 g) were weighed by difference and placed together on to a large glass sheet. The pigment paste and varnish were then mixed together with a palette knife for approximately 15 minutes.

The resulting ink was checked for signs of insufficient mixing. Several portions of ink were drawn down into a thin film on the glass sheet and examined to ensure that the pigment paste had been incorporated properly.

The procedure was repeated for the hydrophobic varnish using the same pigment paste.

It must be noted at this procedure necessarily introduces a component of varnish which will be common to the HL and HB inks. The extent of this common varnish, being of the order of one third of the total varnish, will tend to reduce the relative difference between the inks. This is seen in Figs 17 and 18.

3.4 Model fountain solutions

Demineralised water has been used as the simplest model fountain solution for the reasons outlined in section 1.5. In addition, demineralised water with isopropyl alcohol added at varying amounts was also used. The isopropyl alcohol GPR was supplied by Merck.

3.5 Low shear rate mechanical stirrers

Two low shear rate mechanical stirrers were used during the course of this work.

Firstly, a simple mechanical stirrer powered by a Citenco motor was used for the off-line emulsification studies based upon the Surland emulsification test method. A fixed four-vaned stirrer paddle was designed to stir the viscous materials (Fig 9). The dimensions of the blades of the stirrer paddle were 30 mm in diameter and 10 mm in depth.

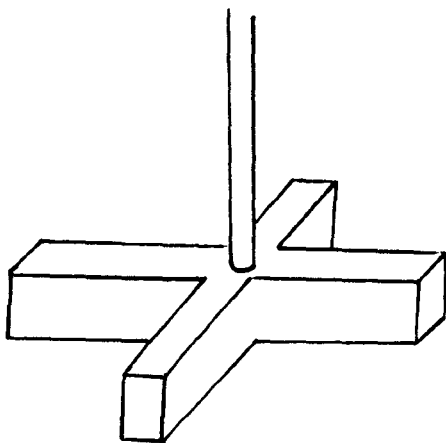


Fig 9 An illustration of the four-vaned stirrer paddle

Initially, the length of the stirrer shaft was 200 mm. However, it was found that this stirrer did not give reproducible results when used in the off-line emulsification studies. This problem was thought to be a result of inefficient mixing caused by mechanical energy - generated by the stirrer motor - being dissipated by the side to side motion of the stirrer shaft.

In order to overcome this, the length of the stirrer shaft was reduced to 100 mm. This configuration was found to give good reproducibility at a stirrer speed of 850 rpm which was calibrated with a tachometer (revolution counter).

Additionally, a Moulinex hand-held stirrer was used as the disperser in the initial experiments examining the size and distribution of water droplets in the fountain solution/varnish emulsions. The stirrer had two pre-set speeds, of which 900 rpm was the one used.

3.6 Dispermat laboratory stirrer

The Dispermat CV laboratory stirrer was used for the high speed, high shear rate studies (Fig 10 and Fig 11). The Dispermat has two main advantages over the conventional mechanical stirrers used in this study.

Firstly, the instrument can reach speeds of up to 20,000 rpm where the peripheral speeds of the impeller can exceed the range of those reached on the press e.g. a sheet-fed press which reaches speeds of up to 10 ms^{-1} .

Secondly, the device maintains a constant pre-set speed, even if the viscosity of the system being stirred is altered. Although the speeds of the conventional stirrers were set, it is unlikely that they actually achieved those speeds when in contact with the varnish or ink. However, it must be noted that under the controlled temperature conditions at which these experiments were conducted, the results from the conventional stirrers are comparable and are still valid.

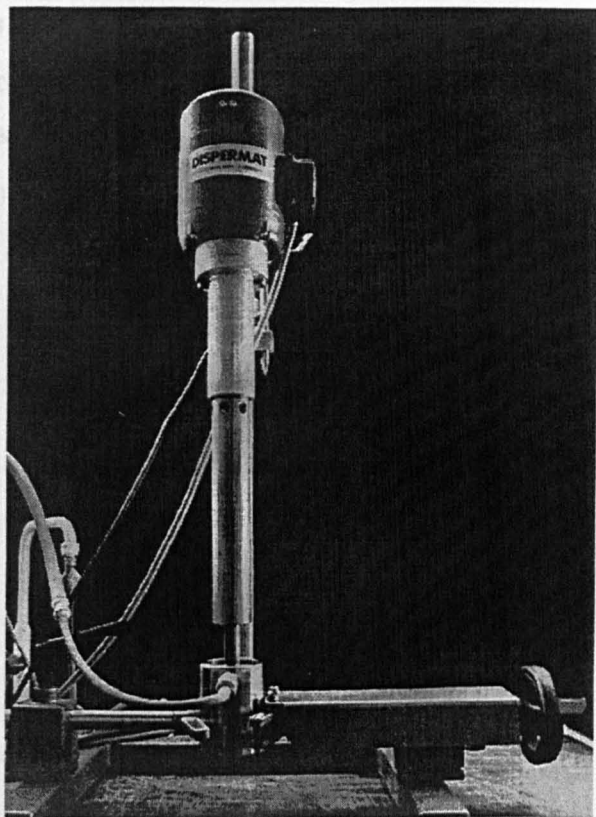


Fig 10 The Dispermat Laboratory stirrer with the stainless steel beaker clamped in place

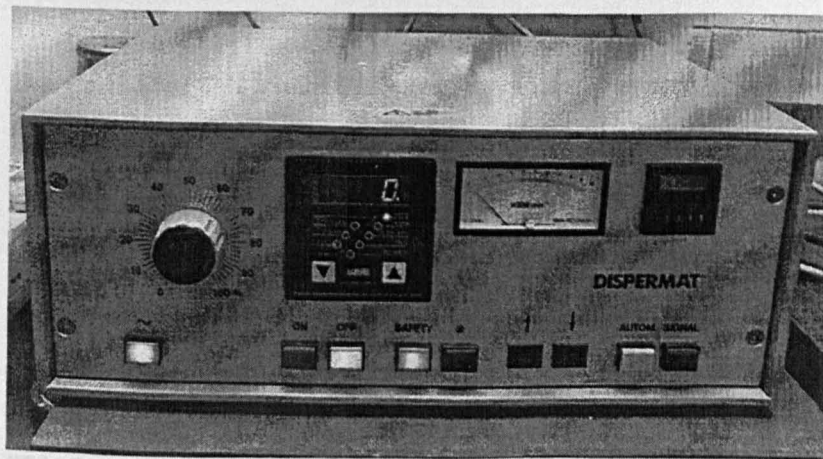


Fig 11 The control box for the Dispermat CV

The Dispermat is said to be operating efficiently as a disperser when a 'doughnut' configuration is formed as the material is being stirred⁴⁸. For the varnish systems this was optimised at 9000 rpm. This was obtained using a high speed disc impeller 20 mm in diameter (Fig 12) which gave a peripheral speed of approximately 10 ms^{-1} ; this is comparable to the speed of a sheet-fed press.

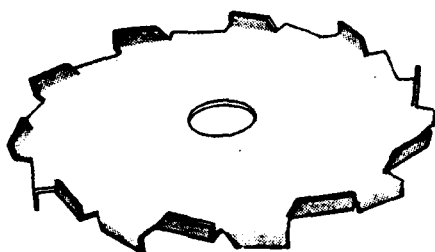


Fig 12 A high speed impeller

The stirrer was used with a 125 cm^3 double-walled stainless steel beaker 55 mm in diameter. This beaker had the facility for circulating water around the inner vessel in order to control the temperature of its contents.

3.7 Carri-Med CSL 100 Rheometer

The Carri-Med CSL controlled stress rheometer was used with a cone and plate geometry for the rheological studies (Fig 13 and Fig 14). The instrument was used to characterise the flow and creep behaviour of the inks, varnishes and their emulsions with fountain solutions. Unless stated otherwise, experiments were carried out at 23°C . The flow experiments were carried out with a cone of 2 cm diameter and a 1° cone angle, whereas the creep experiments were carried out with a 2 cm diameter cone and a 2° cone angle.

This instrument is software-driven which enables experiments to be carried out under identical conditions within a series.

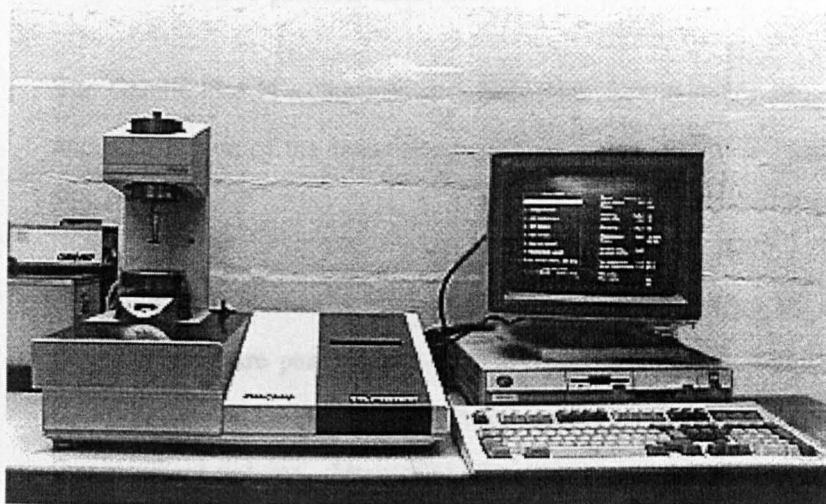


Fig 13 The Carri-Med CSL 100 Rheometer

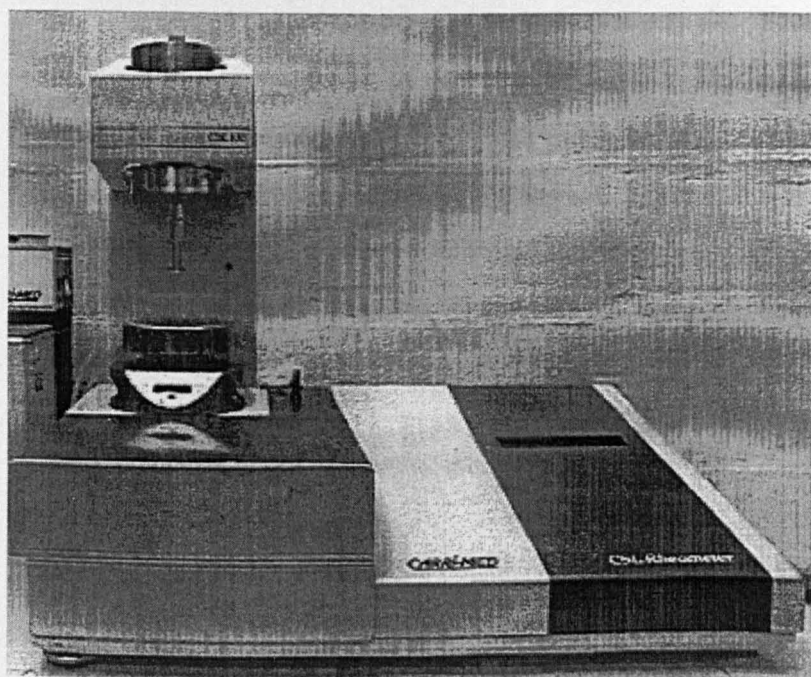


Fig 14 Detail of the cone and plate of the Carri-Med CSL 100 Rheometer

3.8 Galai CIS-1 particle analyser

The Galai CIS-1 is a computerised inspection system which was used to determine the size and distribution of the water droplets dispersed in the model varnish systems (Fig 15 and Fig 16)

The Galai CIS-1 uses a time-size mapping system based on the 'Time of Transition' theory to measure particle size directly. A helium-neon laser beam is scanned circularly by a rotating wedge prism and focused down to a 1.2 micron spot which scans the sample measurement volume. Interaction signals are generated as the laser intersects the particles within the sample measurement volume. These signals are picked up by a detector and the information is processed automatically through a statistical software programme.

As the laser beam rotates at a constant speed, the duration of interaction provides a direct measurement of the cross-section of each droplet/particle. Several thousand particles are measured during the period of data acquisition (i.e. 30-40 seconds). In addition to the above, a video camera is incorporated into the instrument which allows the visual inspection of the droplets/particles on a separate monitor as they are being scanned. Each sample was placed in a 10 x 10 mm cuvette with xylene GPR (m.w. 106.17, supplied by Merck), and a small magnetic stirrer bar, in order to measure the dispersed water droplets.

3.8.1 Preparation of xylene for use with the Galai CIS-1

Xylene was selected as the medium for the particle size studies because it dissolved the varnish while leaving the water droplets suspended in the varnish/xylene medium. Before use, the xylene was shaken together with demineralised water in a small powder jar in order to saturate it. The mixture was allowed to separate into two distinct layers with the upper layer being xylene.

3.3.2 Preparation of samples for the Galai CIS-1



Fig 15 The Galai CIS-1 particle analyser

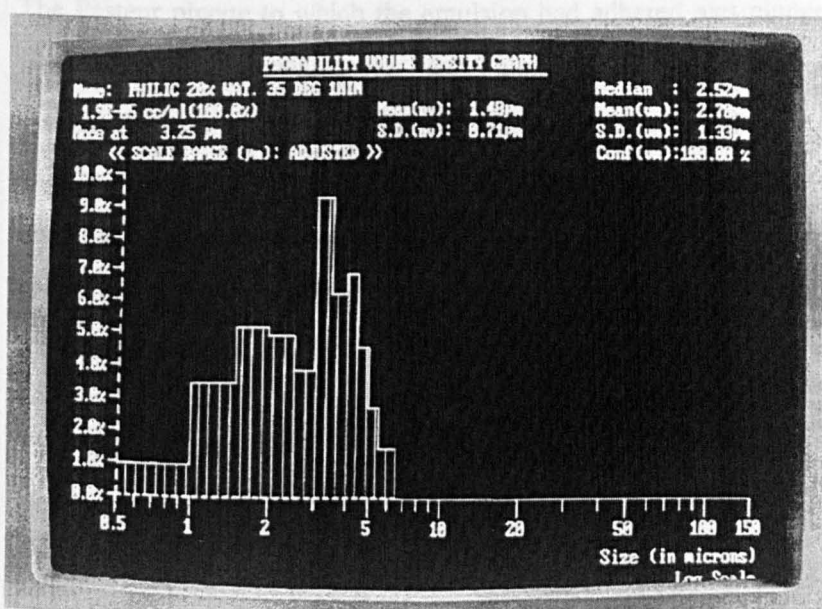


Fig 16 Detail of the computer screen showing a droplet distribution graph

3.8.2 Preparation of samples for the Galai CIS-1

A clean cuvette (containing a magnetic stirrer bar) was filled with the 'water-saturated' xylene. The cuvette was then placed in the Galai CIS-1 and checked to ensure that there were no detectable water droplets present. If water droplets were present within the detection limits of the machine, the xylene was discarded and a fresh sample was examined. If the xylene was found to contain a negligible amount of suspended water it was used for the determination of the droplet size distribution in the fountain solution/varnish emulsions.

The fountain solution/varnish emulsions were prepared under various specified temperature, rheological and time regimes; details will be given where appropriate.

A small sample of the fountain solution/varnish emulsion was removed by plunging the tip of a glass Pasteur pipette several times into the emulsion to ensure that a uniform sample was obtained. A sample was acceptable if it gave a signal to noise ratio of 0.80-1.

The Pasteur pipette to which the emulsion had adhered was plunged gently several times into the cuvette containing the 'water-saturated' xylene. This allowed the varnish to dissolve in the xylene whereas the water droplets, which had been dispersed in the varnish, became suspended in the varnish/xylene solution. This process was continued until the contents of the cuvette became slightly cloudy (but not opaque). The sampling procedure described enabled the preparation of the very dilute suspensions required for the measurement of droplet size distribution on the Galai CIS-1 particle analyser.

The cuvette was placed in the Galai CIS-1 and its contents were scanned. The simultaneous image of the spherically shaped water droplets being measured was transmitted via the video monitor.

3.9 Drop Volume Dynamic Tensiometer (DVDT)

The Drop Volume method is one of the classical ways of measuring the surface tension and interfacial tension of liquids. Drops of a liquid are allowed to detach themselves slowly from the tip of a vertically mounted narrow tube and they are then either weighed or their volume measured.

The Drop Volume Dynamic Tensiometer (DVDT), which was developed at BP Sunbury, is based upon this method and was used to determine the interfacial tension between the model varnishes and various fountain solutions⁴⁹. In order to measure the interfacial tension accurately by this method, the tip of the tube containing the first phase must be wetted completely by the second phase. This ensures that only the fountain solution/varnish interface is measured.

There are, however, limitations in measuring the interfacial tensions of a system where one of the liquids has a high viscosity. The formation of the drop will be influenced by the high viscosity of the material and the interfacial properties will be masked. Therefore, it is not possible to measure the interfacial tension between the varnish and the fountain solution directly with the DVDT. In order to overcome the constraints placed on the test method by the high viscosity of the varnish systems, it was necessary to dilute the varnish systems with a suitable solvent.

3.9.1 Preparation of varnish/xylene mixture for use with the DVDT

Varnish (10 g) was weighed into a glass beaker. The beaker was then placed on a hot plate and heated to 70°C. Xylene (GPR) (7 cm³) was stirred into the warmed varnish and the mixture was left on the hot plate until the xylene was incorporated fully into the varnish (i.e. approximately 5 minutes).

The beaker was removed from the hot plate and allowed to cool to room temperature (21-23°C).

3.9.2 Procedure for measuring interfacial tension with the DVDT

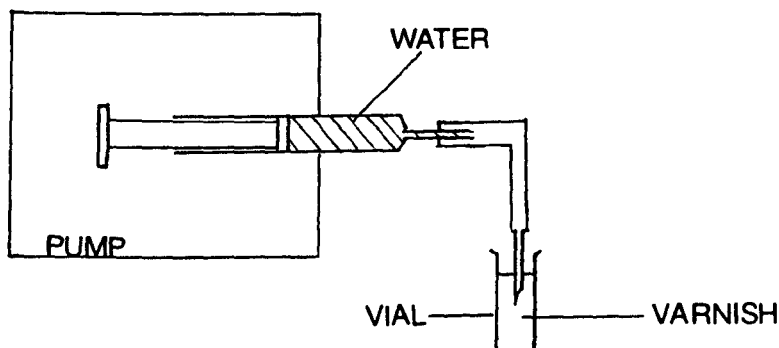


Fig 16a A schematic diagram of the DVDT

The equipment was set up as shown above (Fig 16a). The syringe was filled with demineralised water and any air bubbles within the syringe expelled. The tip of the syringe needle was placed beneath the surface of the diluted varnish, which was contained in a small vial, and then clamped in position. The syringe pump was set to the minimum flow rate at which water droplets would be formed at the tip of the needle (i.e. pump setting 7 or 4.56 mm³s⁻¹). Details of the calibration of the DVDT where the needle tip diameter is 1.463 mm, are given in Table 5. The pump setting and the corresponding flow rates are shown.

Pump Setting	Flow Rate (mm ³ s ⁻¹)
1	0.0456
2	0.091
3	0.228
4	0.456
5	0.91
6	2.28
7	4.56
8	9.1
9	22.8
10	45.6

Table 5. Calibration chart showing the flow rates for the syringe pump (DVDT)

The time taken between one droplet of water forming and the next was measured and recorded. This procedure was repeated a total of three times.

These experiments were carried out under carefully controlled temperature conditions. The vial containing the diluted varnish was suspended in a water bath until it had reached the required temperature. However, in order to see the water droplets being formed it was necessary to raise the vial above the level of the water in the water bath. This introduces a small experimental error which is estimated to be no more than $\pm 1^\circ\text{C}$. This factor was minimised by allowing the contents of the vial to equilibrate between repeated measurements.

The data from this test i.e. the drop formation time, together with the density differential between the oil phase and the water phase and the flow rate were each input into a computerised algorithm which calculated the interfacial tension between the two phases.

III RESULTS AND DISCUSSION

4 Characterisation of model varnish and ink systems

4.1 Off-line emulsification studies

Off-line emulsification studies adapted from the Surland emulsification test were carried out on the model ink and varnish systems; these were used as an initial means of examining the water pick up characteristics of the varnish and ink systems.

4.1.1 Determination of the water pick up characteristics of the model systems

Materials

Hydrophilic varnish

Hydrophobic varnish

Hydrophilic ink

Hydrophobic ink

Demineralised water

Procedure

A clean beaker (50 cm³) was placed on a balance and the varnish or ink (10 g) was weighed in the beaker. The stirrer paddle (designed for use with the Citenco motor) was placed in the beaker and the balance tared. The equipment was set up for stirring and an excess of demineralised water (approximately 10 cm³ taken from a reservoir of 40 cm³) was added to the varnish/ink.

The contents of the beaker were stirred at 850 rpm for one minute.

After stirring, the excess water was decanted off and any remaining loose droplets of water were removed from the fountain solution/varnish mixture by inverting the beaker and shaking it gently until no further water was seen; the varnish or ink remaining

adhered to the inside of the beaker. The beaker, its contents and the stirrer paddle were re-weighed and the difference in weight recorded.

This procedure was repeated on each sample for a total of ten one-minute periods of stirring. The test was repeated three times for each varnish and ink and an average value for the resulting data is reported.

Results

Comparing the water pick up characteristics of the hydrophilic varnish with those of the hydrophobic varnish, it can be seen that the hydrophobic varnish initially absorbs water at a slower rate and appears to reach equilibrium more slowly (Fig 17). Overall, the amount of water absorbed by the hydrophobic varnish was lower than that absorbed by the hydrophilic varnish; however, the total amount of water absorbed after ten minutes of testing was similar.

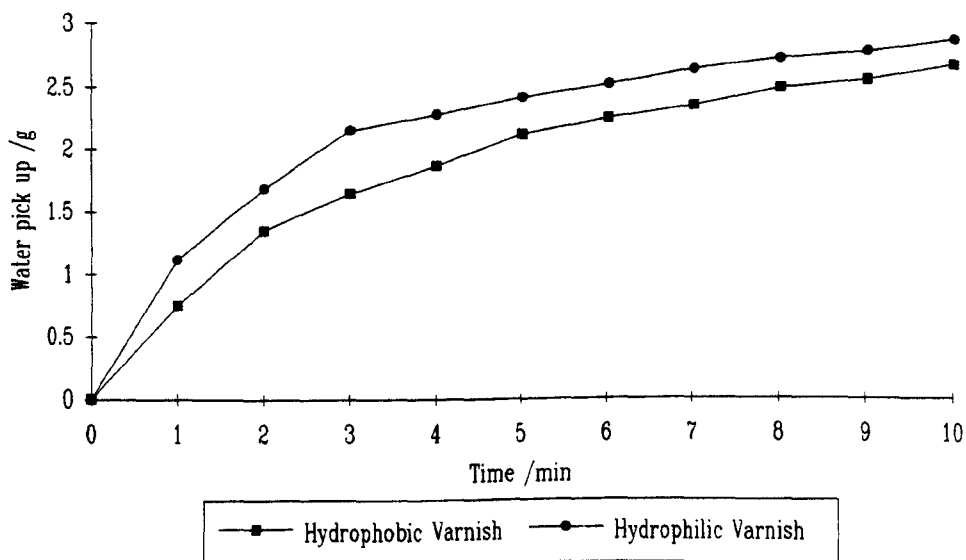


Fig 17 Comparison of the emulsification curves of the hydrophilic and hydrophobic varnishes

The model inks were found to follow similar trends, with the hydrophobic ink absorbing less water at a slower rate than the hydrophilic ink (Fig 18).

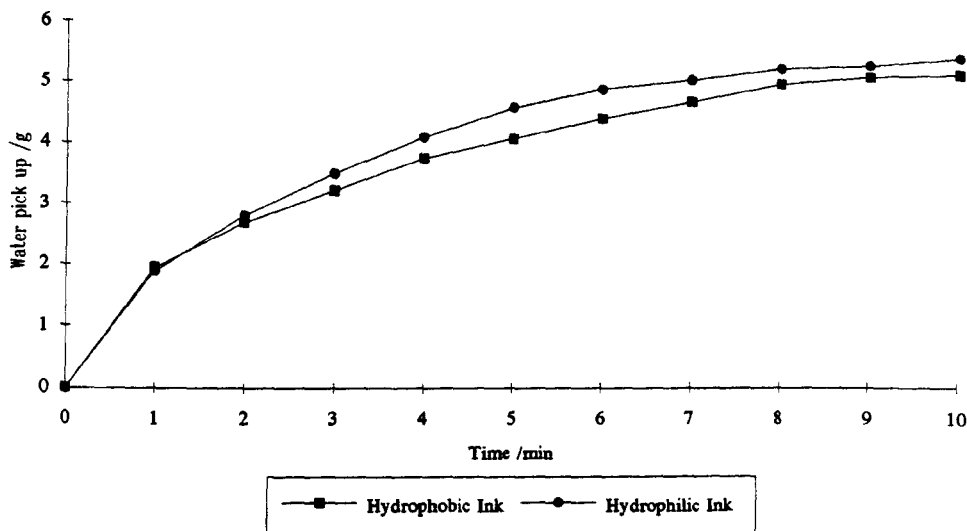


Fig 18 Comparison of the emulsification curves of the hydrophobic and hydrophilic inks

A typical plot of the emulsification data i.e. water pick up (g) versus time (min) shows that a non-linear relationship exists between the variables. In order to overcome the difficulties involved in finding a non-linear model for these systems, the time variable was re-expressed to linearise the data. This was achieved by using the square root of time as the x-variable. The following model was tested:

$$y = A + B * \sqrt{x} + e \quad (15)$$

where A is the intercept, B is the slope and e is a random error. Within this model, significance tests showed A to be insignificant. Therefore the equation may be expressed as:

$$y = B * \sqrt{x} \quad (16)$$

The raw data was fitted to this equation. Figs 19 and 20 show that during the initial four minutes of the test, the water pick up is proportional to the square root of time. After that initial period, the rate of water pick up decreases as the emulsion approaches saturation and the linear relationship no longer applies.

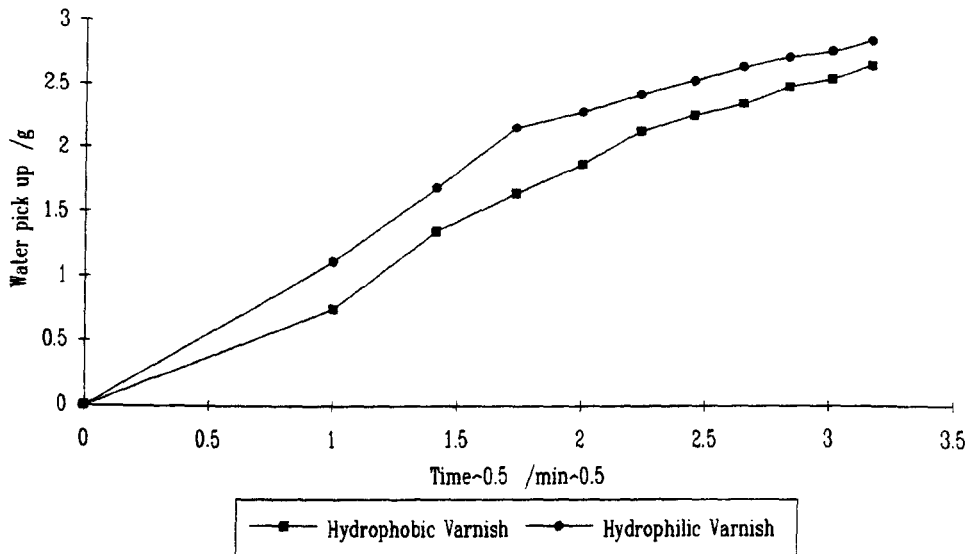


Fig 19 Square root of time v water pick up for the hydrophobic and hydrophilic varnishes

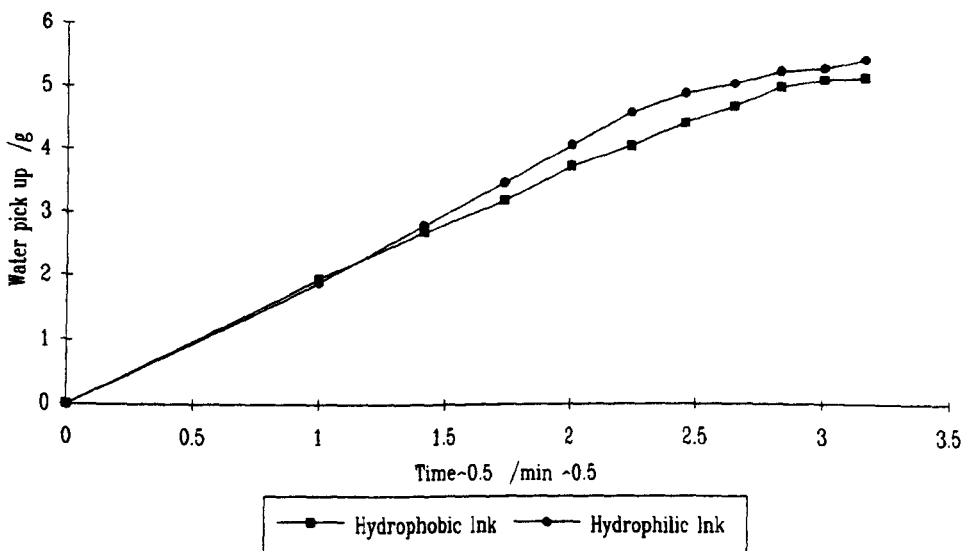


Fig 20 Square root of time v water pick up for the hydrophobic and hydrophilic inks

Comparing the model inks with the model varnish systems, it can be seen that the presence of the pigment affects both the rate and amount of water absorbed (Figs 21 and 22).

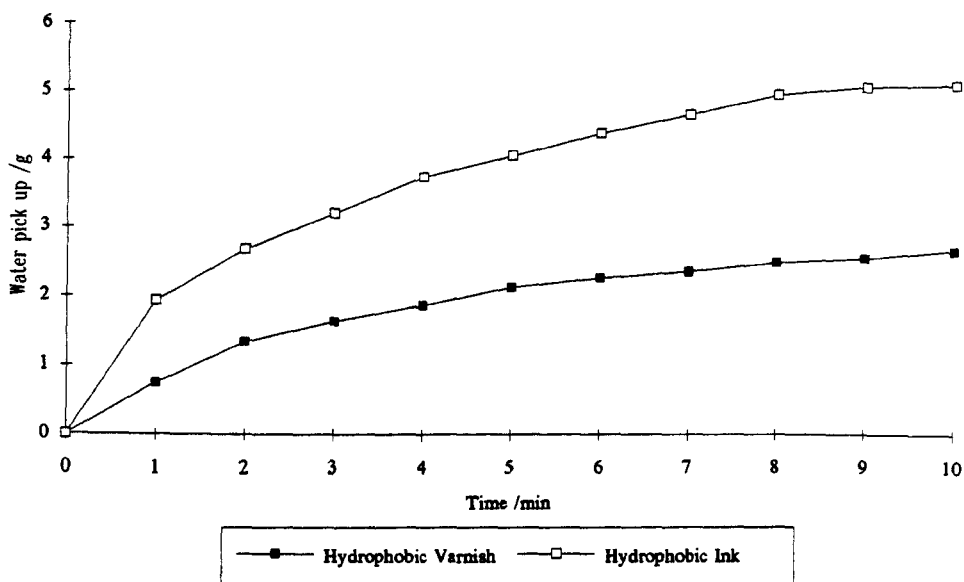


Fig 21 Comparison of the water pick up of the hydrophobic varnish and ink

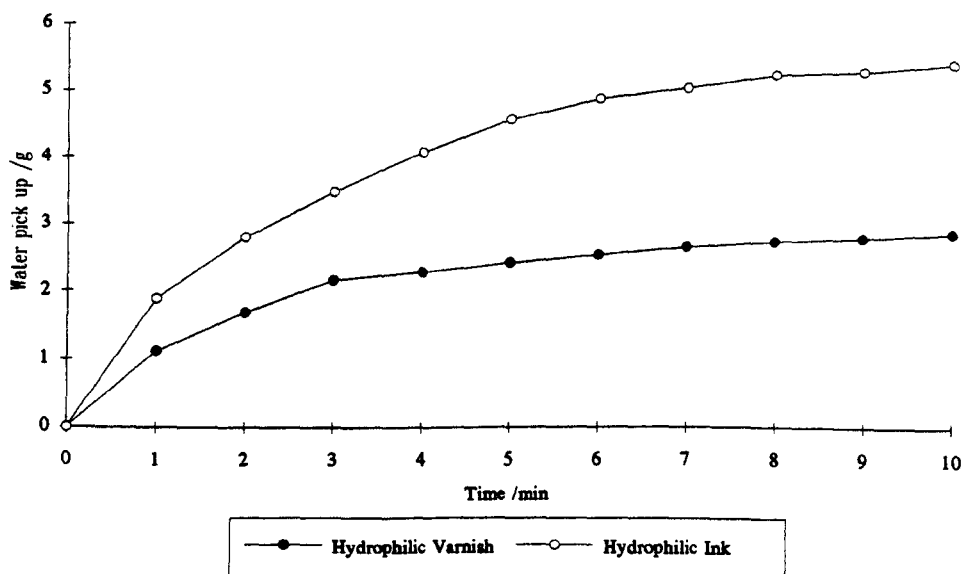


Fig 22 Comparison of the water pick up of the hydrophilic varnish and ink

The rate of water absorbency is higher for both the pigmented inks and the total amount of water absorbed is approximately twice that of the corresponding varnishes. This indicates that the pigment plays a significant role in the mechanism of water uptake. In this respect, note that there is a smaller spread in data points between the two inks compared with the two varnishes (Figs 17 and 18).

The surface of pigment particles are rich in polar moieties and therefore tend to be hydrophilic in nature. Although the pigment particles are sterically stabilised within the varnish by long chain alkyds, some affinity for water appears to be retained which may be responsible for the increased capacity of water uptake of the inks. In view of the above comment on the reduced variations between the inks, it may be that the pigment/varnish/water interactions override the varnish/water interactions.

Abrecht and Heigl⁵¹ found that when pigments of varying hydrophilicity were dispersed in identical vehicles, different quantities of water were emulsified. The ink containing the most hydrophilic pigment was found to absorb the largest amount of water.

However, Braun³⁴ examined a series of pigments in a common varnish base and found that the most hydrophilic pigment gave the lowest water uptake. Further, it was proposed that variations in water pick up were caused by rheological differences arising from the interaction between the pigments and the vehicles. Braun concluded that 'a printing ink with poor flow is a poor matrix for emulsification'.

As the the present study has used the same pigment base in both the model hydrophobic and hydrophilic ink systems, the focus is placed on the role of the varnish system. The results show that the model ink and varnish systems have produced emulsification curves that are characteristic of an 'ideal' or 'PC' curve according to the Surland emulsification test. Most of the water is absorbed within the first 4 minutes of testing. It could therefore be predicted, within the limits of the Surland postulate, that all of these systems would run well on a lithographic press, running at moderate speeds.

Whereas the hydrophobic varnish and the hydrophobic ink absorb less water than their hydrophilic counterparts, the differences between their emulsification curves appear to be small. As the performance of these materials falls within the 'ideal' pattern of behaviour, this would suggest (as far as the Surland test is concerned) that they are more or less indistinguishable from each other. Clearly, this method is not sensitive enough to highlight any differences in behaviour which might be caused by varying the hydrophobicity of the model systems.

4.2 Determination of rheological properties of the model inks and varnishes

Materials

Hydrophilic varnish

Hydrophobic varnish

Hydrophilic ink

Hydrophobic ink

Procedure

The flow and creep behaviour of the above materials were examined according to the parameters set out in section 3.7.

All materials were subjected to similar rheological conditions. The flow behaviour was examined over a three-minute period, with an applied stress ranging from 0 to 4775 Pa; the upper shear stress being limited by the geometry of the measuring system. The creep behaviour was examined over a period of ten minutes.

Results

The data obtained from the creep experiments with the hydrophobic and hydrophilic varnishes (Table 6) showed that both materials gave low instantaneous compliances. This is characteristic of materials which are fairly stiff in consistency and have a resistance to the onset of flow. The varnishes also appear to exhibit behaviour that is characteristic of a viscous fluid. The Newtonian viscosity is within the range expected for materials that would flow, albeit slowly, when shear stress is applied.

	Instantaneous Compliance (m^2N^{-1})	Newtonian Viscosity (Pas)	Newtonian Viscosity Shear Rate (s^{-1})
Hydrophilic Varnish	6.20E-04	1315	1.51E-03
Hydrophobic Varnish	1.22E-03	1783	1.12E-03
Hydrophilic Ink	2.02E-03	559	1.21E-03
Hydrophobic Ink	2.95E-03	891	2.25E-03

Table 6 Creep behaviour of the model varnishes and inks

In general, the flow characteristics of the varnishes was similar in that they exhibited non-Newtonian shear thinning behaviour. The varnishes were also found to be thixotropic in nature. The data from the upward flow curves were fitted to the Herschel-Bulkley model (Eq 17), which is valid when the relationship between shear stress and shear rate is linear. The flow curves and theoretical models are shown in Figs 23-30. It should be noted that the limitations of the printer did not allow different legends to be used for the measured and theoretical curves; however, since the regression of the fitted curves is at least 0.999 there is a large degree of overlap.

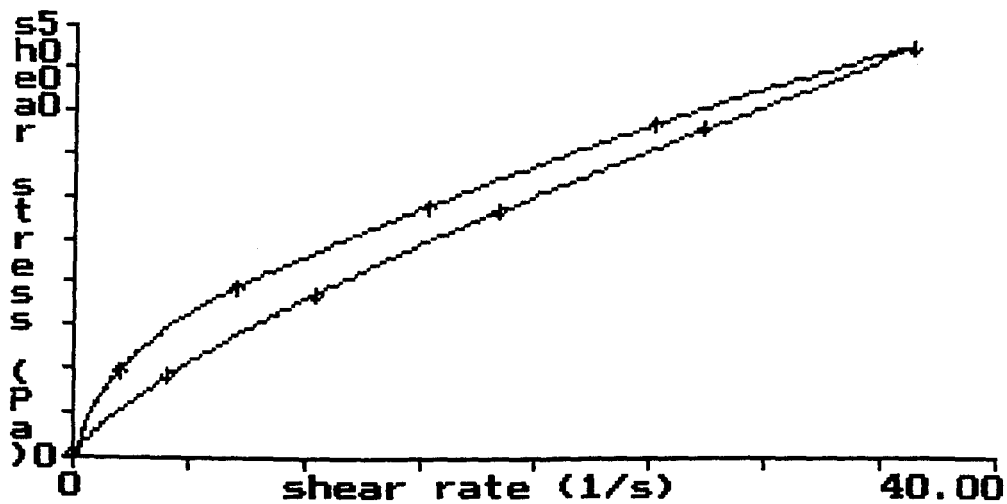


Fig 23 The flow curve of the hydrophobic varnish

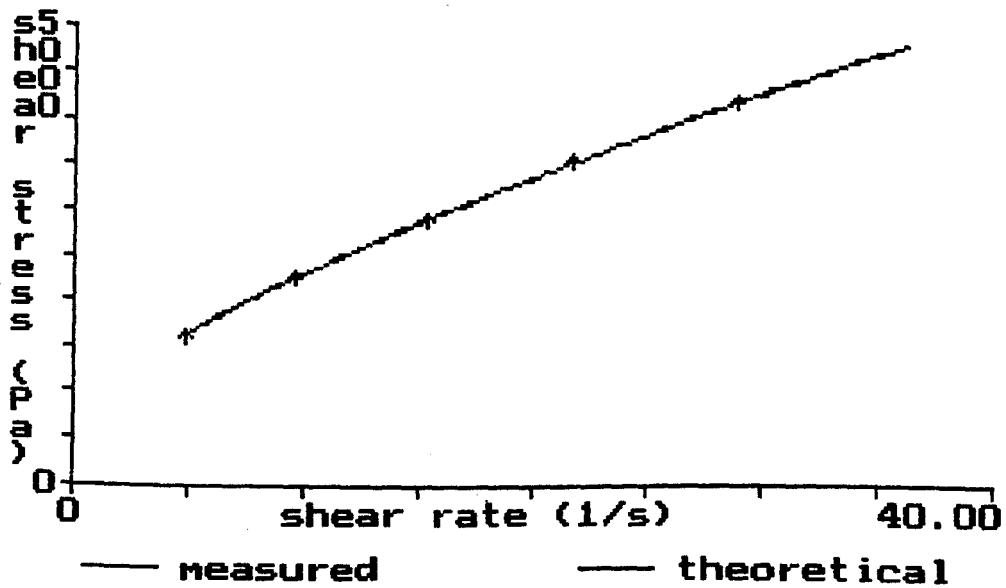


Fig 24 The theoretical upward flow curve of the hydrophobic varnish

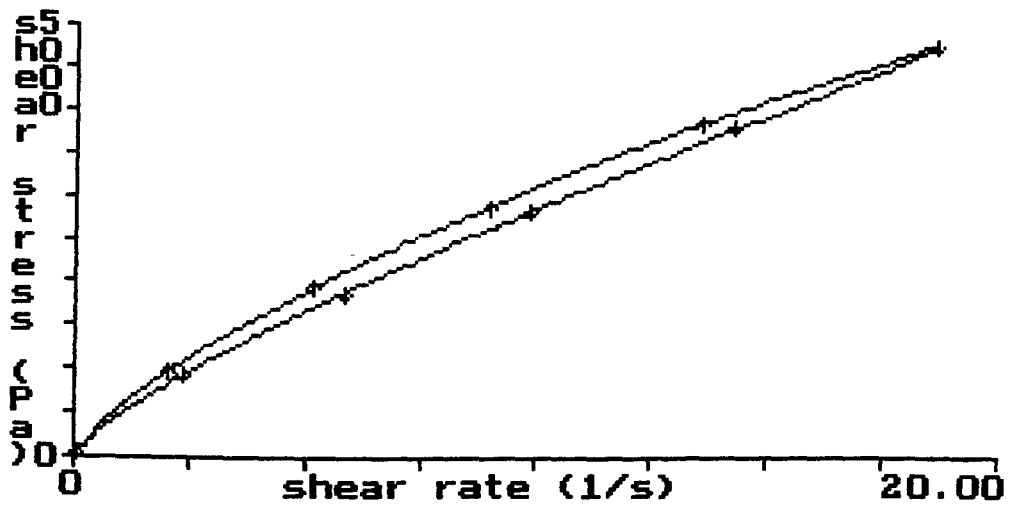


Fig 25 The flow curve of the hydrophilic varnish

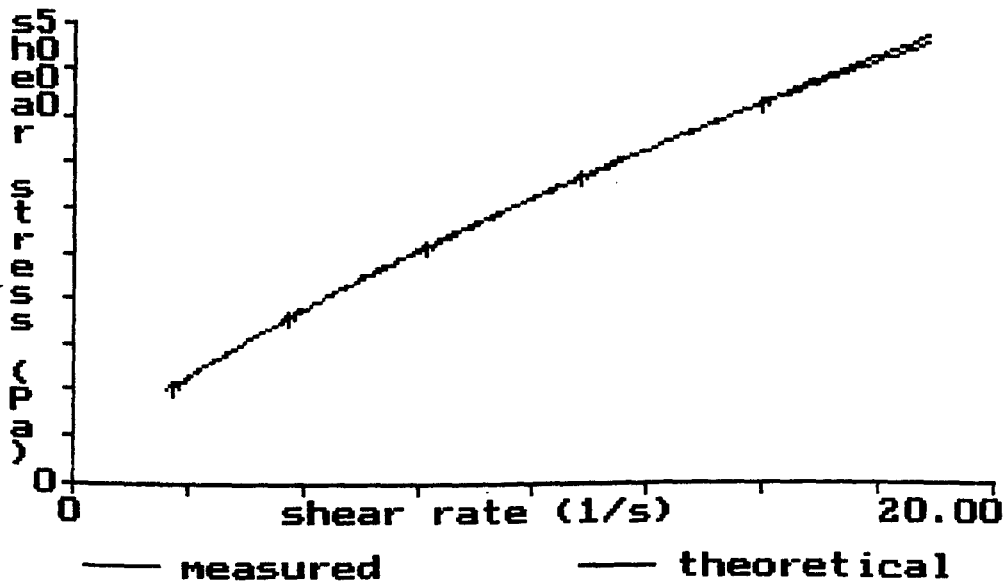


Fig 26 The theoretical upward flow curve of the hydrophilic varnish



Fig 27 The flow curve of the hydrophobic ink

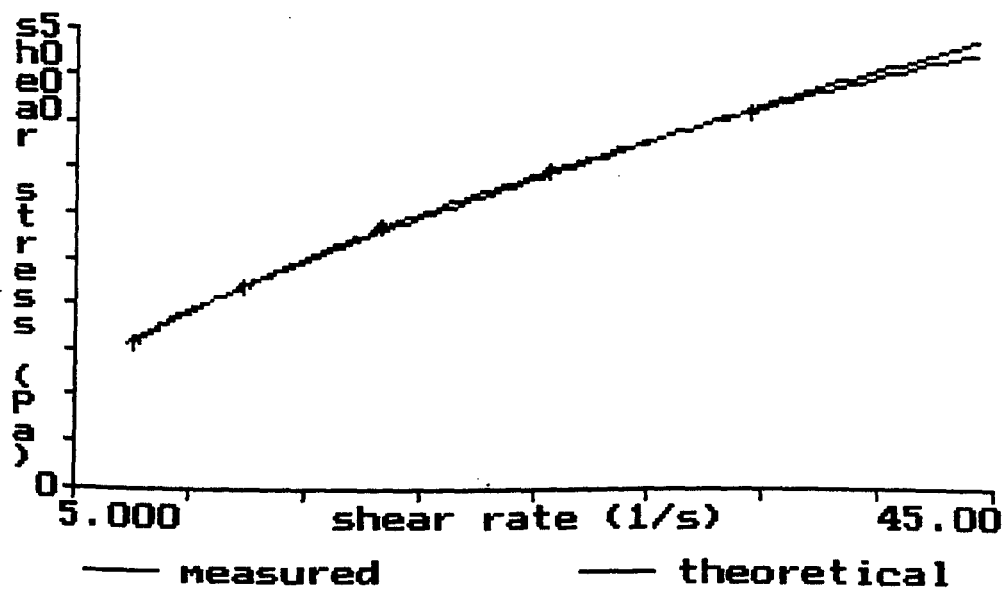


Fig 28 The theoretical upward flow curve of the hydrophobic ink

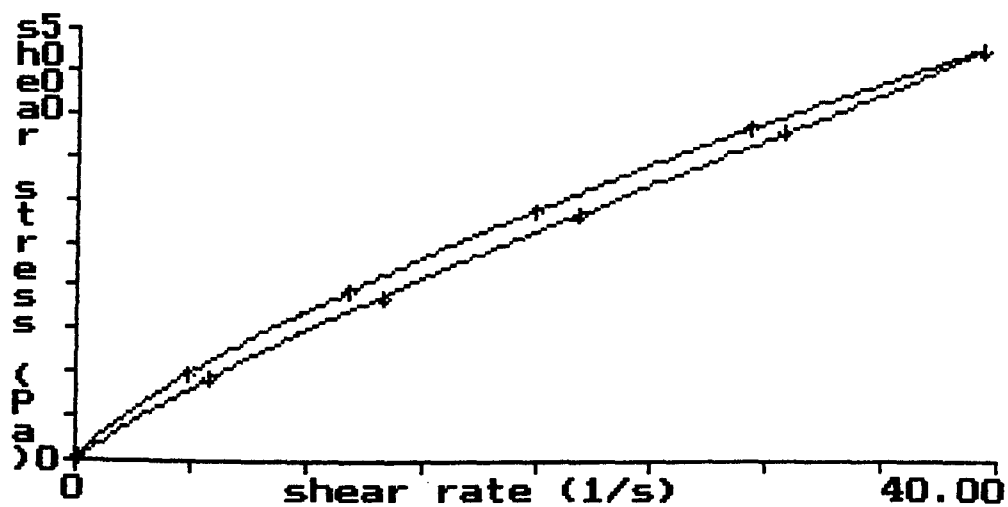


Fig 29 The flow curve of the hydrophilic ink

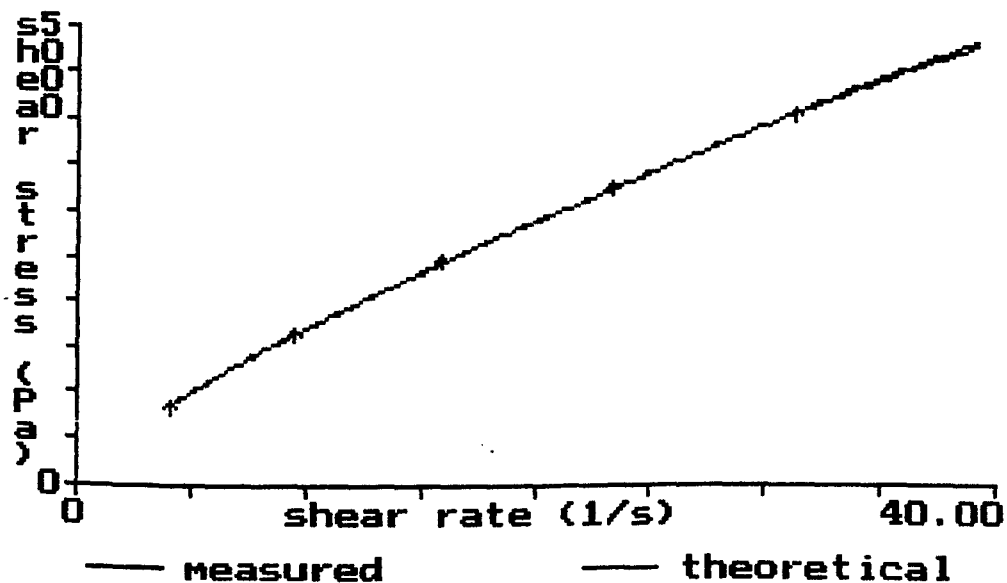


Fig 30 The theoretical upward flow curve of the hydrophilic ink

$$\text{Stress} = A + B * \text{Rate}^C \quad (17)$$

where

A = Calculated yield (Pa)

B = Viscosity coefficient

C = Rate index

The values of A, B and C for the model materials are given in Table 7.

	A	B	C
Hydrophobic varnish	537.2	382.8	0.6706
Hydrophilic varnish	0	605.5	0.7120
Hydrophobic ink	0	470.1	0.6161
Hydrophilic ink	0	303.3	0.7543

Table 7. Table of values for A, B and C from the Herschel-Bulkley model

It was found that the hydrophobic varnish had a greater degree of thixotropy, with the area of thixotropy being calculated at $12610 \text{ Pa}\cdot\text{s}^{-1}$ compared with $3580 \text{ Pa}\cdot\text{s}^{-1}$ for the hydrophilic varnish. A similar comparison applies for the model inks

The hydrophobic and hydrophilic inks were found to have similar compliances to their corresponding varnishes, but their Newtonian viscosities are lower which suggests that there is a greater degree of mobility within the inks (Table 6). There are no major differences in the instantaneous compliances (which is to be expected) because the presence of pigment particles should not greatly affect the rheology of the varnish; however, in this case, the pigment particles appear to have enhanced the flow characteristics of the corresponding inks.

The hydrophobic and hydrophilic inks have exhibited non-Newtonian shear thinning behaviour and were thixotropic. In fitting the data to the Herschel-Bulkley model, the trends shown by the varnishes were repeated in the corresponding inks. The hydrophobic ink has a thixotropic area of 20500 Pas^{-1} compared with 7634 Pas^{-1} for the hydrophilic ink. The presence of the pigment particles appears to have had the effect of approximately doubling the area of thixotropy for the model inks in comparison to the model varnishes. This implies a bigger change in structure.

Overall, the apparent viscosities of the hydrophobic and hydrophilic inks were lower than those of the corresponding varnishes. Given that the pigment particles are generally asymmetrical, this result may be expected. It is known that the addition of such particles alters the flow properties of the material in which they have been dispersed. If the pigment particles have formed aggregates, an increase in shear rate will result in a reduction of the amount of fluid immobilised by the particles and lead to a reduction in the apparent viscosity. However, as the pigment particles are pre-wetted in the formation of the pigment flush, before being incorporated into the varnish, it is possible that the reduction in the apparent viscosity occurs as a result of the increased disturbance of the flow lines throughout the ink.

4.2.1 Determination of the effects of water concentration on emulsion stability

Materials

As in 4.1.1

Procedure

The ink/varnish (10 g) was weighed into a clean glass beaker (50 cm³). Demineralised water (0.5 g) was added dropwise from a graduated 1 cm³ pipette to the ink/varnish while stirring at 850 rpm. Stirring was continued for three minutes.

The emulsion was allowed to rest for a period of ten minutes before rheological assessment. This allowed the emulsion to recover from the shearing process. The high viscosity of the emulsion was sufficient to prevent coalescence and settling during this 'rest period'.

The flow behaviour was examined under the conditions stated in section 3.7; however, an extended testing time of ten minutes was used to examine the shear stability of the emulsion.

The creep behaviour was examined according to the conditions outlined in section 3.7. The creep curves are shown in Appendix 1.

This procedure was repeated for water concentrations of 0, 10, 15, 20 and 25% (w/w).

Results

In comparing the flow curves of the demineralised water/hydrophobic varnish emulsions (Fig 31), it can be seen that at a water concentration of 5% the emulsion remains stable during the experiment. At water concentrations of 10 and 15%, the emulsions have similar initial stability; however, they are beginning to show signs of instability after approximately 160 seconds. At 20% water, the emulsion begins to show signs of instability after approximately 125 seconds, whereas at 25% water the emulsion breaks down after 110-115 seconds. At this point, the cone of the rheometer spins freely with very little resistance. It can therefore be concluded that phase separation has taken place and the cone is in contact with a film of water and not the composite emulsion.

The shear rate against time curves for the water/hydrophobic ink emulsions (Fig 32) appear to have similar stability at 5 and 10% water, whereas the emulsions at 15 and 20% water are similar to each other but are tending towards instability after 150-155 seconds. With 25% water the emulsion is less stable and breaks down at 100-110 seconds, duplicating the results seen in the hydrophobic varnish.

The shear rate against time curves of the water/hydrophilic varnish emulsions (Fig 33) show that all the emulsions have similar stability with no definite time-dependent pattern being established.

The corresponding water/hydrophilic ink emulsions behave in a similar manner between 5 and 20% water concentration but at 25% water the emulsion appears to be moving towards instability after 100 seconds (Fig 34).

The effective shear rates in the hydrophobic varnish and ink systems are almost an order of magnitude higher than those in the hydrophilic systems. This indicates that there is a greater degree of slippage and lower shear stability in the hydrophobic systems.

Fig 31 Shear rate v time curves of the hydrophobic varnish with 0-25 % water

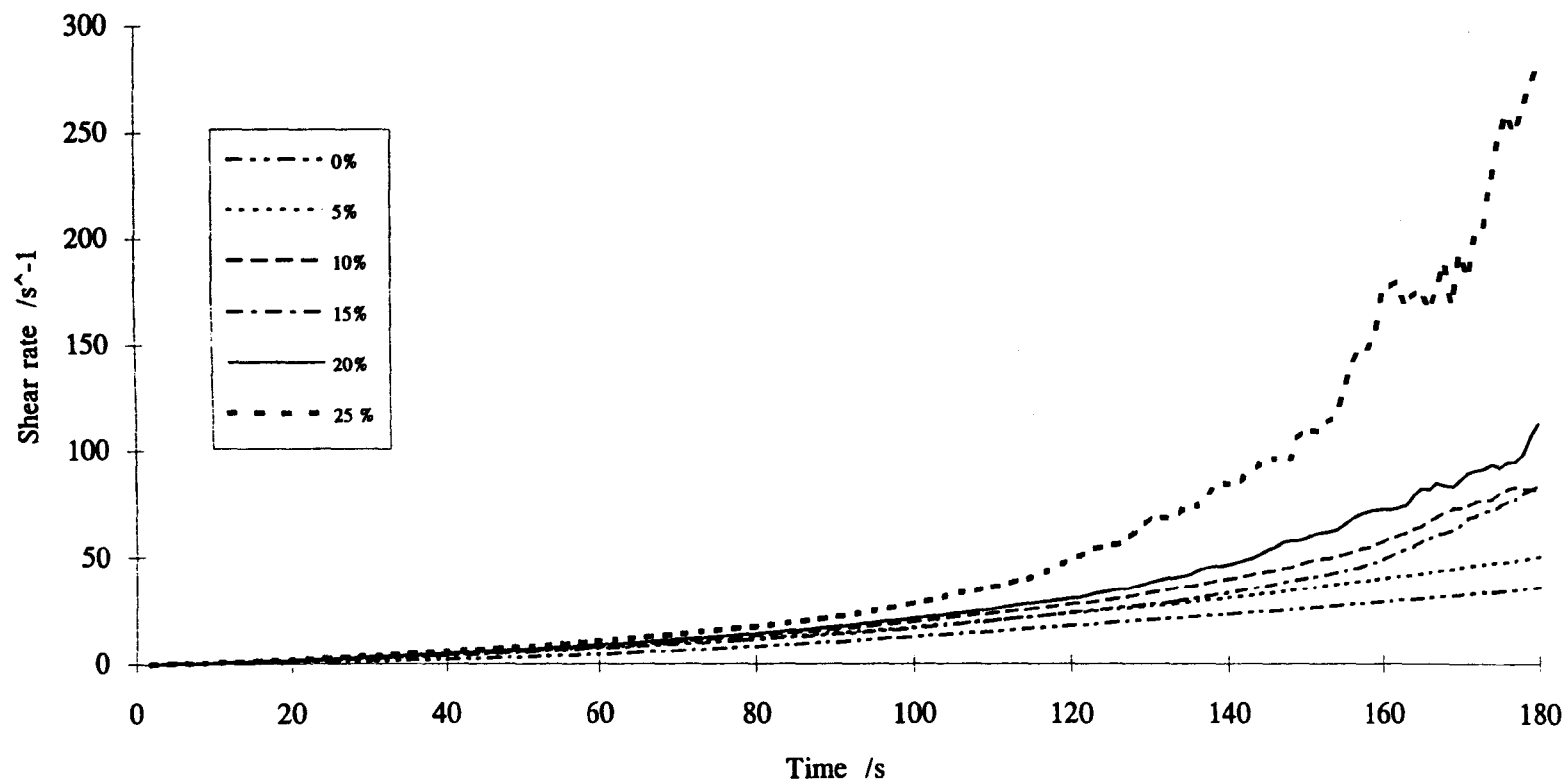


Fig 32 Shear rate v time curves of the hydrophobic ink with 0-25% water

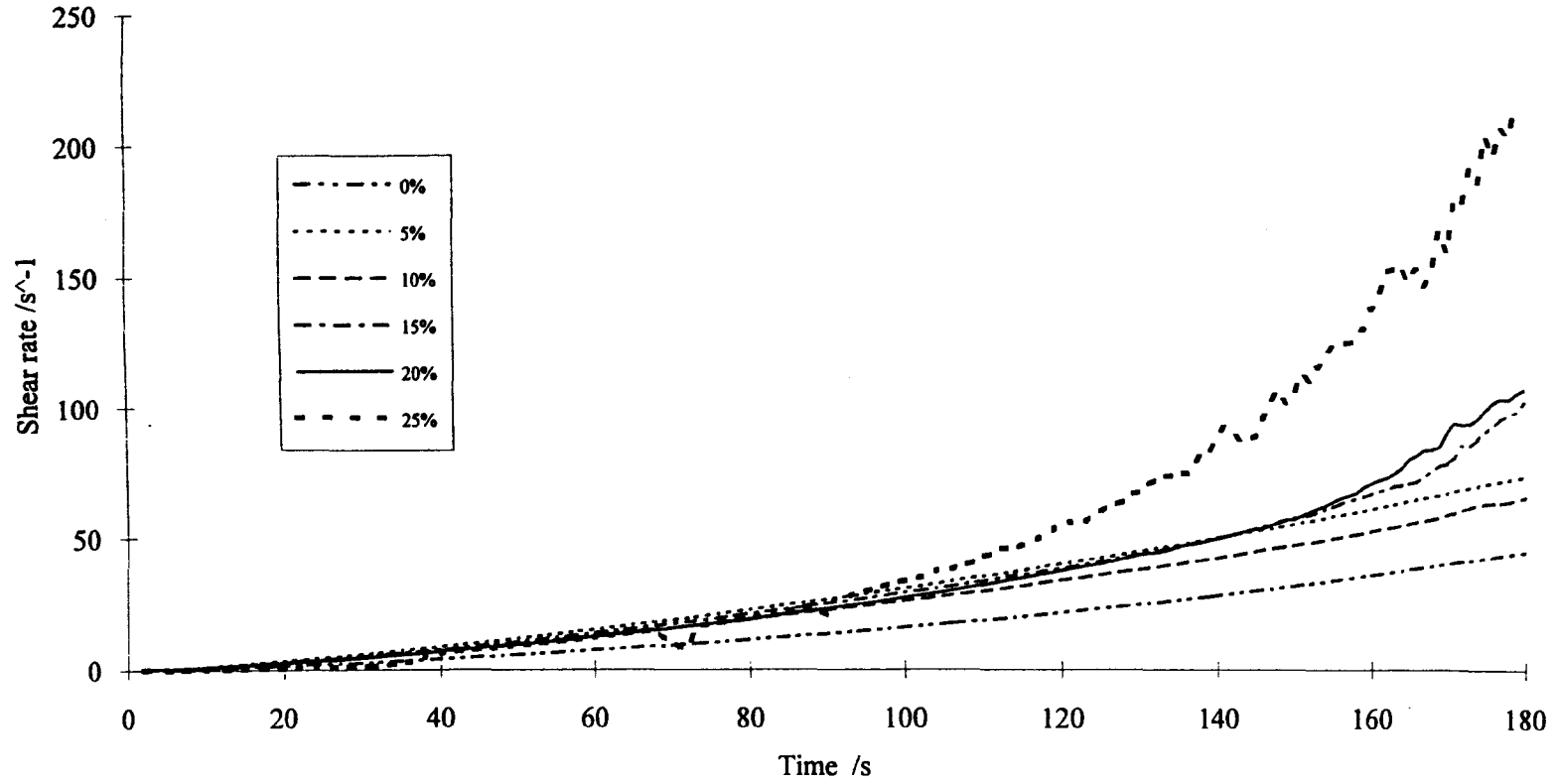


Fig 33 Shear rate v time curves of the hydrophilic varnish with 0-25% water

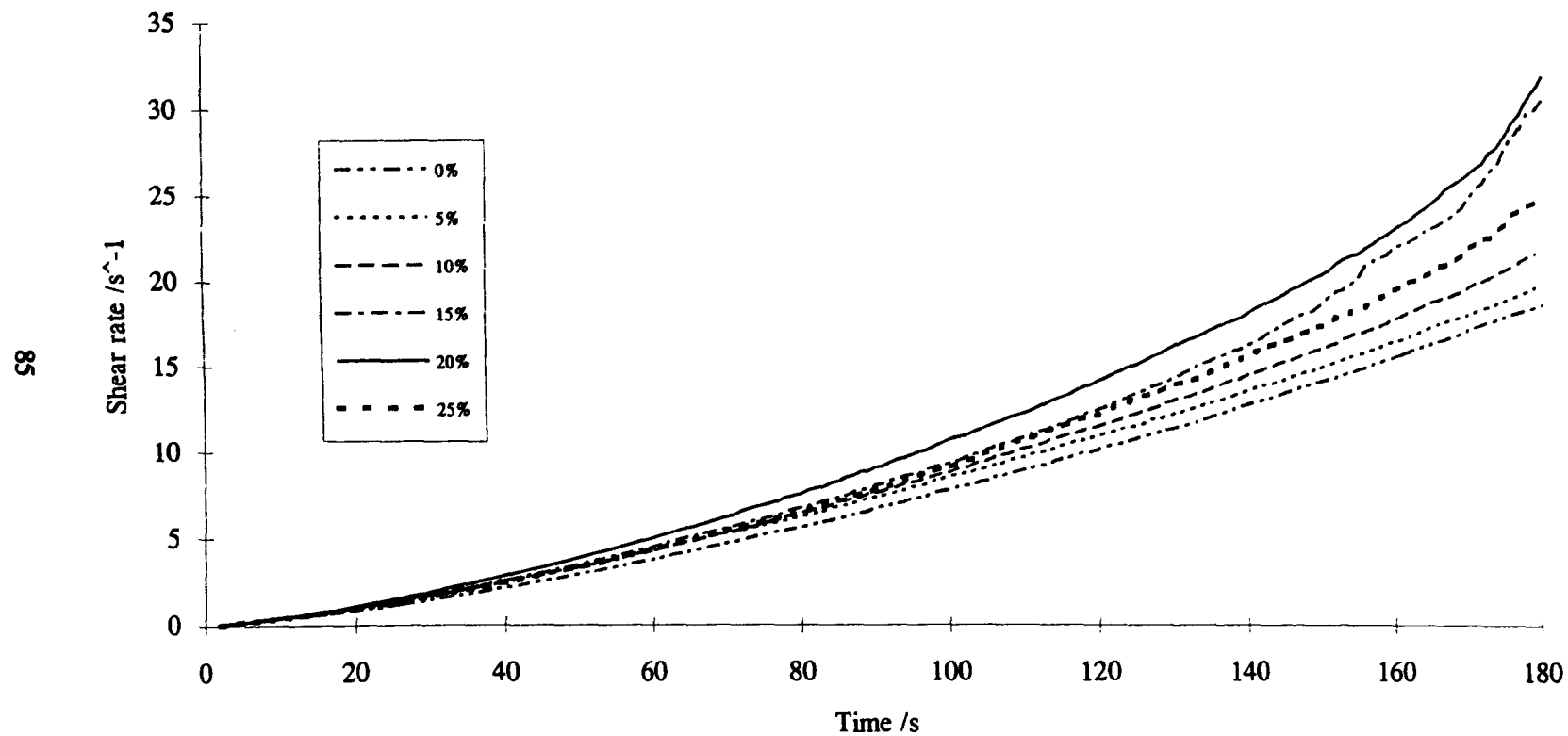
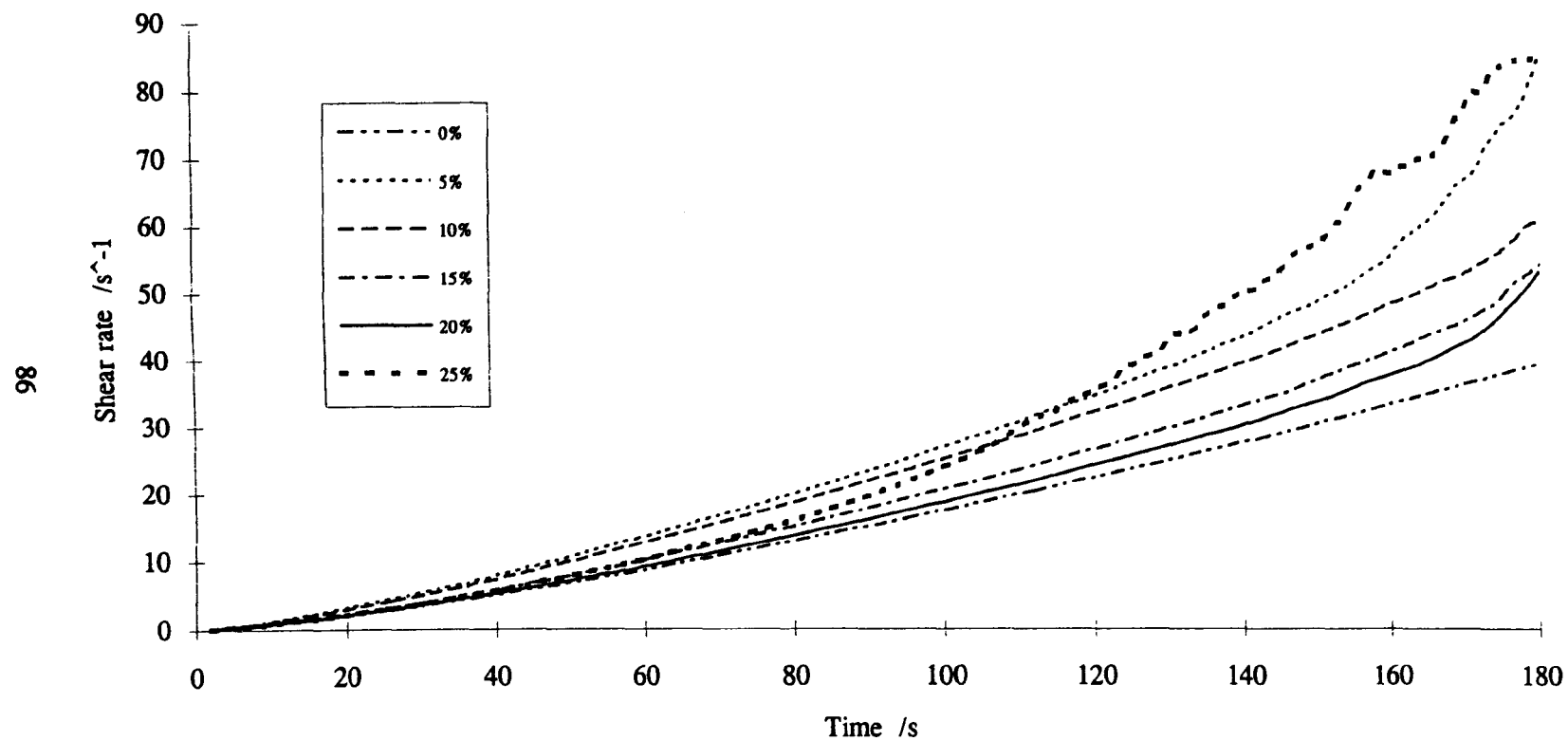


Fig 34 Shear rate v time curves of the hydrophilic ink with 0-25% water



The data from the creep experiments are shown in Table 8 and the curves are shown in Appendix 1. The hydrophobic varnish emulsions gave similar instantaneous compliances (i.e. $1-2\text{E-}3$) and similar Newtonian shear rates (i.e. $1-1.6\text{E-}3$) for all concentrations of water. The Newtonian viscosities of the varnish emulsions were generally lower than those of the neat varnish, indicating that the mobility of the water/varnish emulsions was greater than that of the relevant varnish.

The water/hydrophilic varnish emulsions have similar instantaneous compliances (i.e. $6-9\text{E-}4 \text{ m}^2\text{N}^{-1}$) and similar Newtonian shear rates to the neat varnish (i.e. $1.5-1.9\text{E-}3 \text{ s}^{-1}$). The Newtonian viscosities of the emulsions are lower than the neat varnish; this is similar to the observations made for the hydrophobic varnish.

The creep behaviour of the hydrophobic ink system showed that the emulsions have similar instantaneous compliances and Newtonian shear rates to the neat ink. However, the Newtonian viscosities which are in the range of 686-948 Pas are lower than those of the corresponding varnish (i.e. 1036-1783 Pas). This indicates that the hydrophobic ink and its emulsions are more mobile than the corresponding varnish.

Similar trends are seen in the emulsions of the hydrophilic ink with instantaneous compliances and the Newtonian shear rates being similar. The Newtonian viscosities which are in the range of 467-665 Pas are also lower than those of the corresponding varnish systems (i.e. 1017-1315 Pas).

The fact that all the demineralised water/varnish emulsions generally gave lower Newtonian viscosities compared with the corresponding varnishes is of interest. According to Einstein's theory for the dispersion of sub-micron spherical particles in a continuous phase, it could be expected that an increase in the number of particles will lead to an increase in the bulk viscosity. However, this theory assumes that there is no slippage within the emulsified system which would allow anomalous flow within the 'disperse phase'. Such slippage constitutes a failure in the rheological measurements.

Table 8 Comparison of the creep behaviour of the model varnish and ink systems containing 0, 5, 10, 15, 20 and 25% demineralised water

Water Concentration (%)	Hydrophilic Varnish					
	0	5	10	15	20	25
Instantaneous Compliance (m^2N^{-1})	6.25E-04	9.37E-04	7.97E-04	6.25E-04	8.33E-04	6.74E-04
Newtonian Viscosity (Pas)	1315	1017	1092	1071	889	1262
Newtonian Shear Rate (s^{-1})	1.52E-03	1.97E-03	1.83E-03	2.25E-03	2.24E-03	1.58E-03
Water Concentration (%)	Hydrophobic Varnish					
	0	5	10	15	20	25
Instantaneous Compliance (m^2N^{-1})	1.21E-03	1.69E-03	2.11E-03	1.83E-03	1.22E-03	1.67E-03
Newtonian Viscosity (Pas)	1783	1132	1370	1225	1036	1191
Newtonian Shear Rate (s^{-1})	1.12E-03	1.77E-03	1.46E-03	1.63E-03	1.93E-03	1.68E-03
Water Concentration (%)	Hydrophilic Ink					
	0	5	10	15	20	25
Instantaneous Compliance (m^2N^{-1})	2.02E-03	1.59E-03	1.36E-03	2.47E-03	1.74E-03	9.84E-04
Newtonian Viscosity (Pas)	555	514	467	506	665	557
Newtonian Shear Rate (s^{-1})	3.58E-03	3.89E-03	4.29E-03	3.96E-03	3.01E-03	3.73E-03
Water Concentration (%)	Hydrophobic Ink					
	0	5	10	15	20	25
Instantaneous Compliance (m^2N^{-1})	2.95E-03	2.48E-03	2.44E-03	1.25E-03	2.25E-03	2.51E-03
Newtonian Viscosity (Pas)	891	686	710	755	948	852
Newtonian Shear Rate (s^{-1})	2.25E-03	2.91E-03	2.82E-03	2.649E-3	2.11E-03	2.35E-03

In the demineralised water/model varnish systems being investigated, one could assume that because of the relative hydrophobicity of the varnishes (compared with the hydrophilicity of the demineralised water), some slippage would occur. Under these circumstances, it would be predicted that the greater the degree of hydrophobicity in the continuous phase (relative to the disperse phase), the greater the slippage.

The data are consistent with this theory in that all concentrations under 15% yield Newtonian viscosities which are lower than those for the neat varnish or ink.

At 20% water, however, the data show considerable variability with a dramatic drop for the varnishes and increases for the inks.

At 25% water, these "dramatic changes" have settled down. Clearly, the systems have a degree of instability in the range of 15-25% water concentration.

Overall, it can be seen that the emulsions of the hydrophobic varnish and the hydrophobic ink become less stable with increasing concentrations of water. However, it is difficult to establish any patterns for the effects of water concentration on the emulsions of the hydrophilic varnish and the hydrophilic ink. Whereas the presence of water affects the rheology and shear stability of the emulsions of all the materials tested, it is clear that the hydrophobic systems are affected to a greater degree. In terms of the water balance concept, it can be said that the hydrophobic systems are more 'sensitive' (or less tolerant) to the presence of water than the hydrophilic systems.

4.3 Further investigation of the emulsification of the model varnish systems

The rheological studies have indicated that generally, the hydrophobic varnish forms emulsions that have a lower stability to shear than the hydrophilic varnish. It is of particular interest that these trends are evident at similar concentrations of water.

An observable effect of the degree of stability of an emulsion is the changes in particle size distribution of the disperse phase. Considering the time effects of the Surland method, it is thought that a more informative approach to examining the key phenomena of emulsification should involve a study of the particle size distributions of the water droplets with respect to the stirring time⁵²⁻⁵⁵. A series of experiments were carried out to examine the extent of emulsification in terms of the water droplet size and distribution.

The effect of temperature on the emulsification process was also investigated. Measurements were carried out on emulsions formed at 70°C and 40°C. These temperatures are typical of those reached on a fast moving press, with the higher temperature being generated by the shear forces involved in the flow of ink through the nip, including cavitation and ink film splitting.

4.3.1 Determination of the extent of emulsification using droplet size analysis

Materials

Hydrophilic varnish

Hydrophobic varnish

Demineralised water

Procedure

Hydrophilic varnish (30 g) was weighed into a 50 cm³ powder jar. The jar was covered with 'parafilm', placed in a water bath at 70°C and allowed to acclimatise for a minimum of 45 minutes.

Demineralised water (3 g), heated to 70°C, was added to the varnish and the two phases stirred together with a Moulinex hand blender at 900 rpm for 20 seconds. At this point, the resulting emulsion was a mustard yellow colour and appeared to be of uniform appearance. A small sample of the emulsion was removed and the particle size distribution determined with the Galai CIS-1 particle analyser, according to the procedure given in section 3.8.2.

The emulsion was stirred for a further 40 seconds (giving a cumulative stirring time of 1 minute). Another sample of the demineralised water/varnish emulsion was removed and examined using the Galai CIS-1.

The process was repeated to yield particle size results at the cumulative stirring times of 2, 3, 4, 5, 6 and 8 minutes. The experiment was ended when the mean particle size appeared to be approaching an equilibrium value.

This procedure was repeated for the demineralised water/hydrophobic varnish emulsion. In this case, the sampling times were after 1, 2, 4, 7, 10, 13 and 16 minutes of stirring.

Both model varnish systems were subjected to the above procedure at 40°C. However, the fountain solution/hydrophilic varnish emulsion was sampled between 1 and 5 minutes of stirring, whereas the fountain solution/hydrophobic varnish emulsion was sampled between 2 and 7 minutes.

Graphs of mean droplet diameter against stirring time the were plotted.

Results

At both temperatures it can be seen that the mean diameter of the water droplets within the emulsions has decreased with increasing stirring time. There is a decrease in the number of large droplets, accompanied by an increase in the number of smaller droplets.

At 70°C, the water droplets within the fountain solution/hydrophilic varnish emulsion appear to be approaching a dynamic equilibrium size, with a droplet diameter of approximately 20 microns after 8 minutes of stirring (Fig 35). In comparison, the breakdown of water droplets in the hydrophobic varnish appears to be nearing a dynamic equilibrium after 10 minutes of stirring with a mean droplet diameter of approximately 25 microns after 13 minutes of stirring.

Examination of the droplet size distributions shows how the size distribution varies with increasing stirring time. For the hydrophilic varnish emulsion, it can be seen that, generally, droplets above 50 μm in diameter disappear, whereas the number of droplets below 10 μm increases (Figs 37-44). The hydrophobic varnish emulsion follows a similar pattern (Figs 45-51).

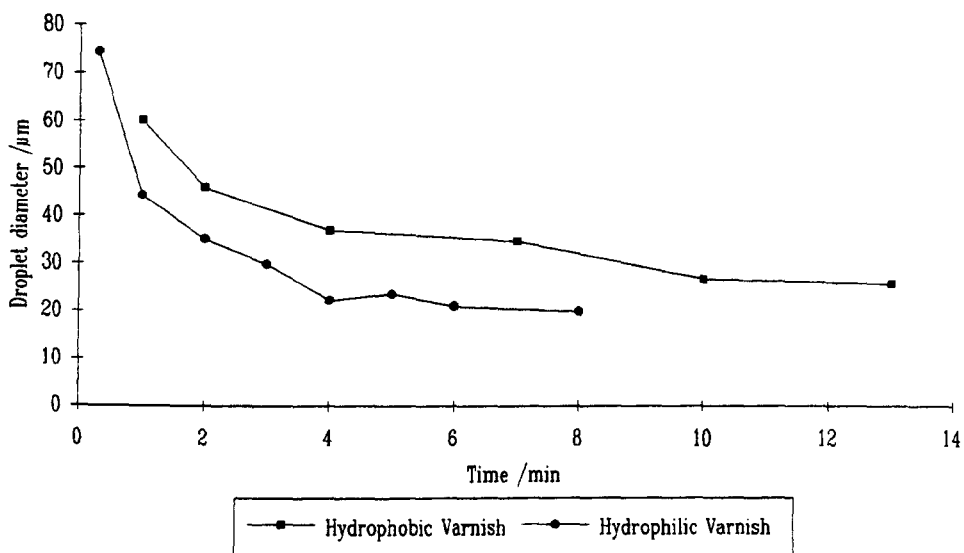


Fig 35 Breakdown of water droplets in the hydrophilic and hydrophobic varnishes at 70°C

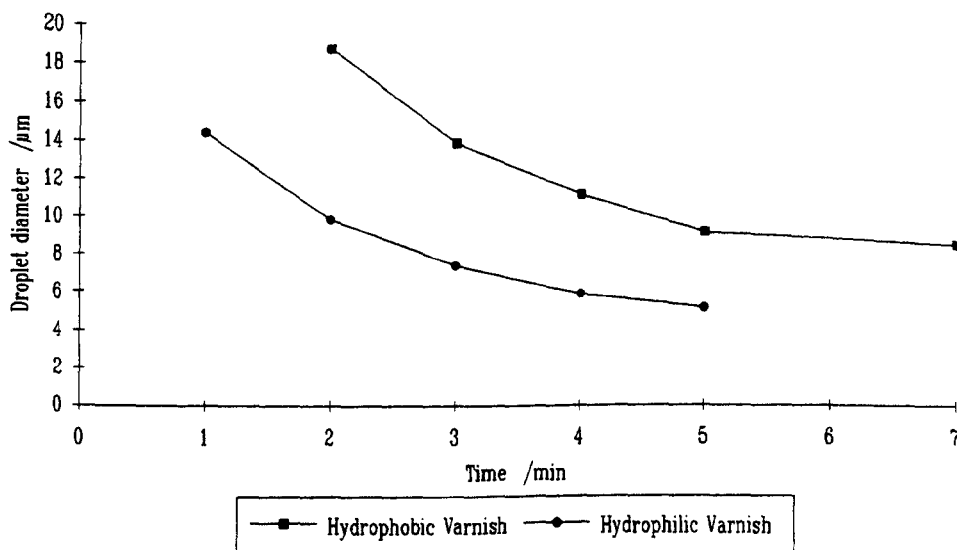


Fig 36 Breakdown of water droplets in the hydrophilic and hydrophobic varnishes at 40°C

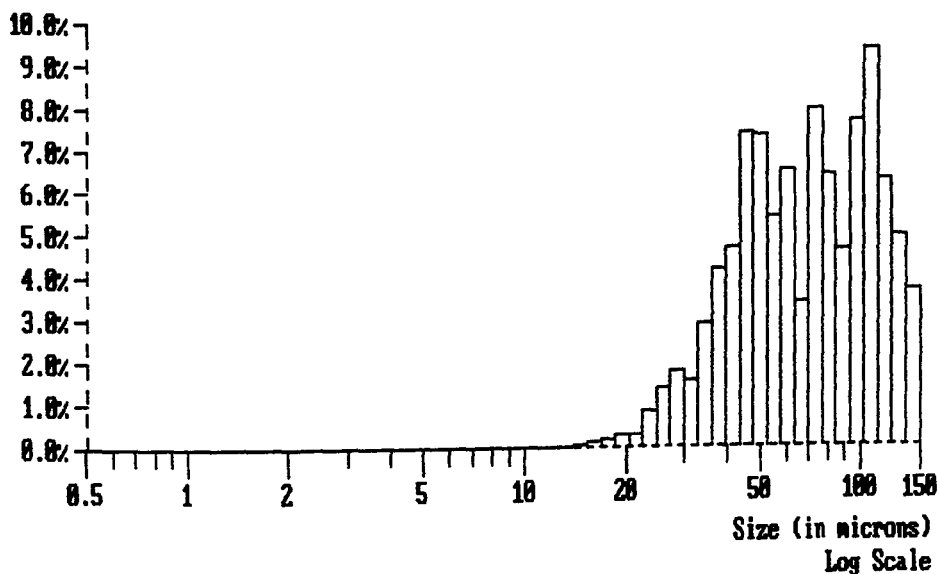


Fig 37 Droplet distribution of hydrophilic varnish
after stirring for 20 seconds at 70°C

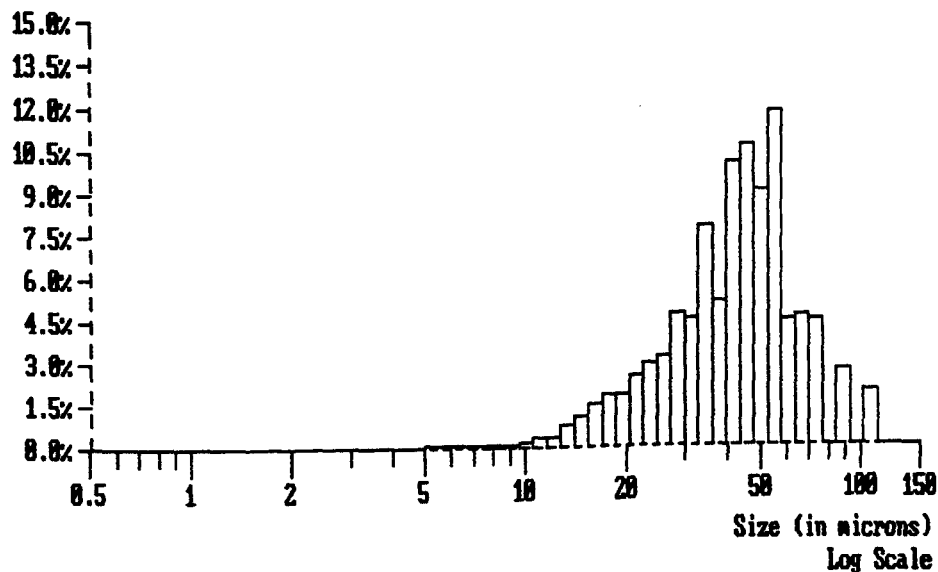


Fig 38 Droplet distribution of hydrophilic varnish
after stirring for 1 minute at 70°C

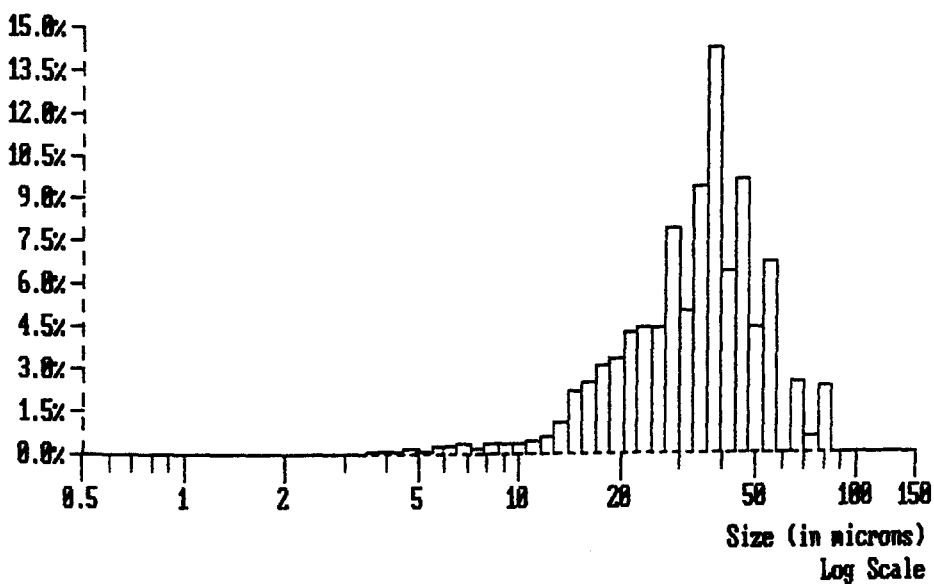


Fig 39 Droplet distribution of hydrophilic varnish
after stirring for 2 minutes at 70°C

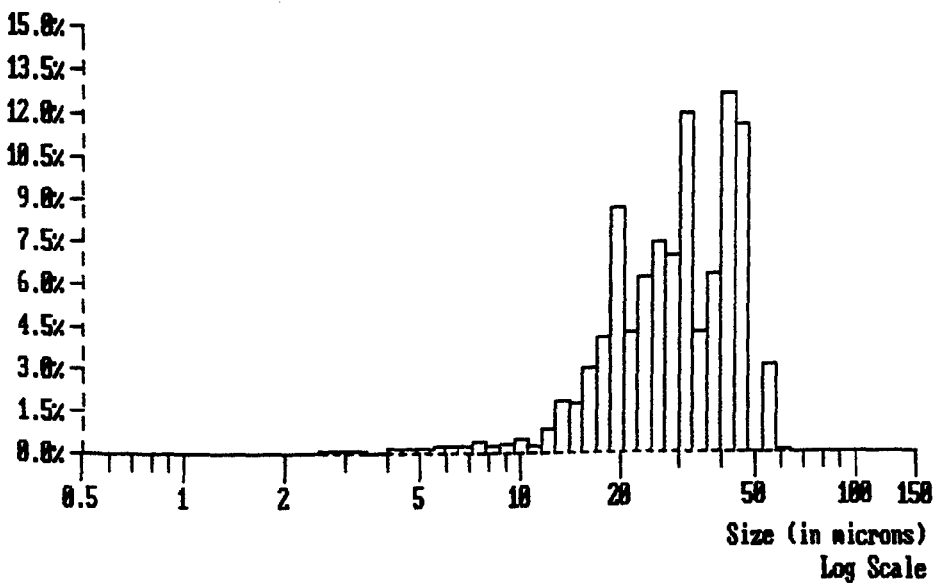


Fig 40 Droplet distribution of hydrophilic varnish
after stirring for 3 minutes at 70°C

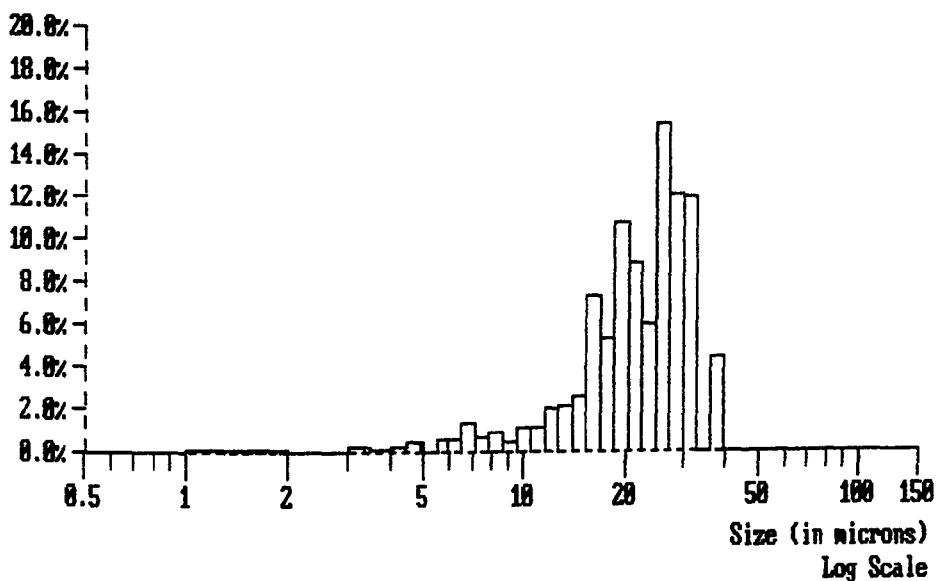


Fig 41 Droplet distribution of hydrophilic varnish
after stirring for 4 minutes at 70°C

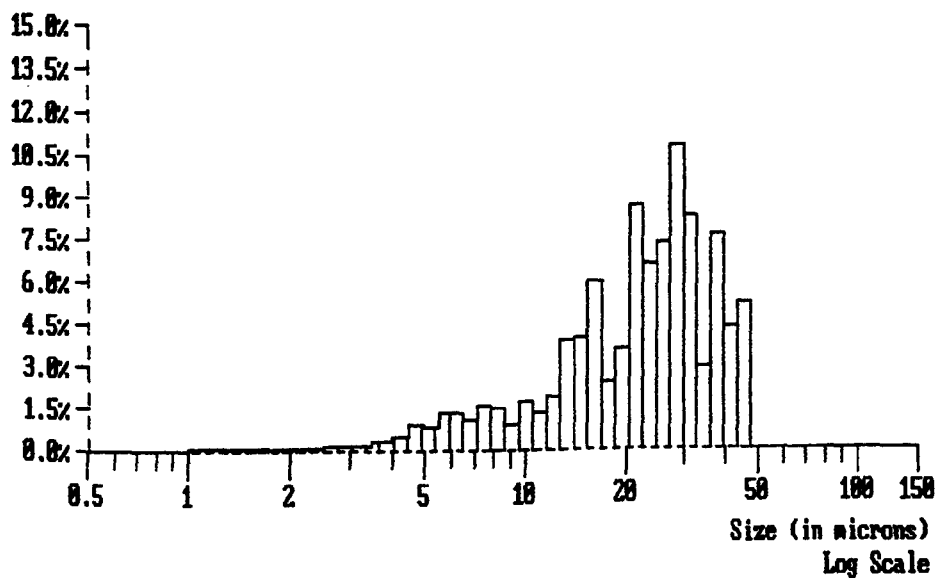


Fig 42 Droplet distribution of hydrophilic varnish
after stirring for 5 minutes at 70°C

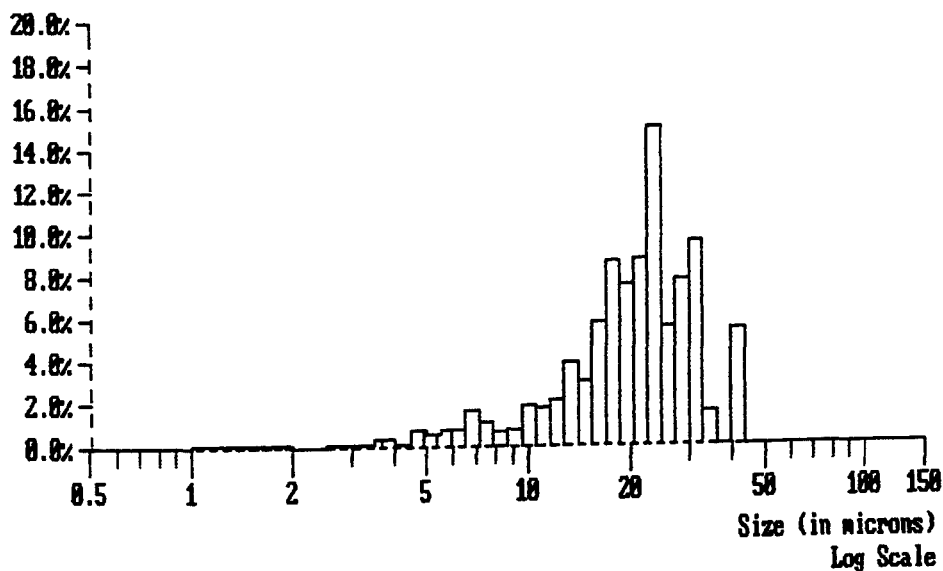


Fig 43 Droplet distribution of hydrophilic varnish
after stirring for 6 minutes at 70°C

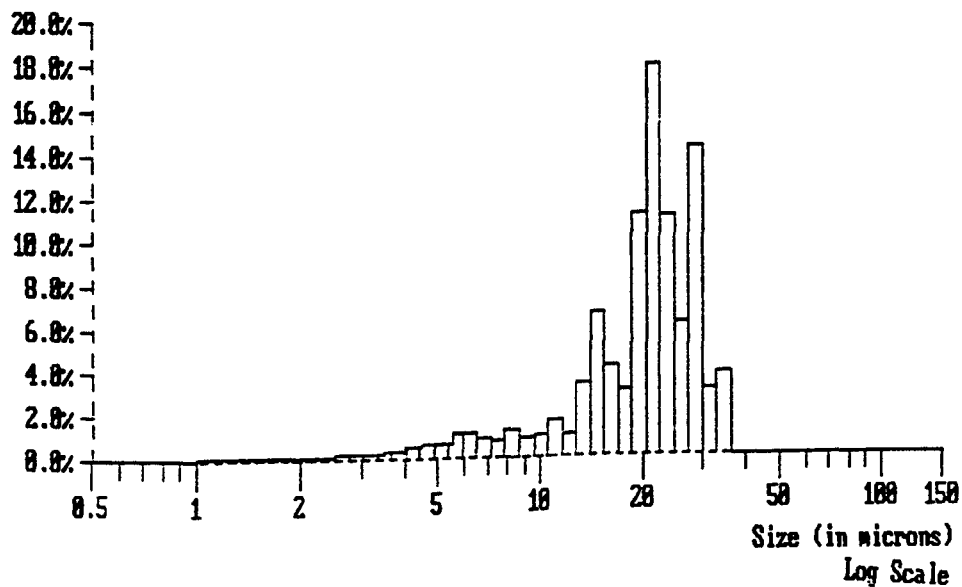


Fig 44 Droplet distribution of hydrophilic varnish
after stirring for 8 minutes at 70°C

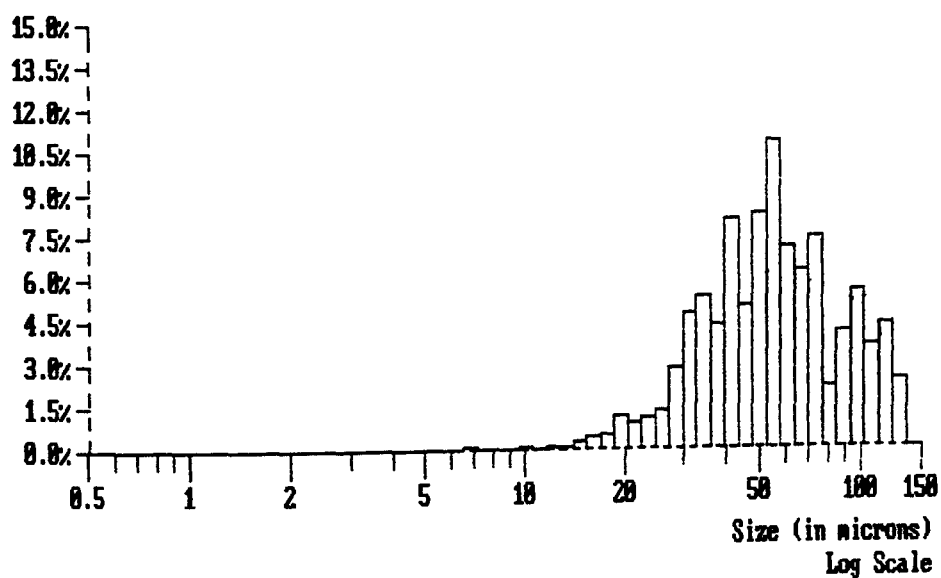


Fig 45 Droplet distribution of hydrophobic varnish
after stirring for 1 minute at 70°C

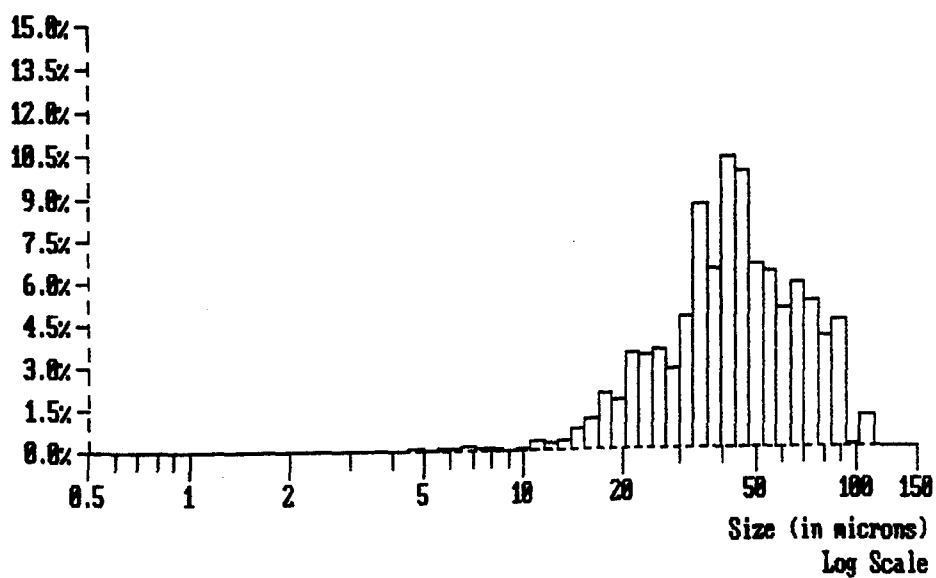


Fig 46 Droplet distribution of hydrophobic varnish
after stirring for 2 minutes at 70°C

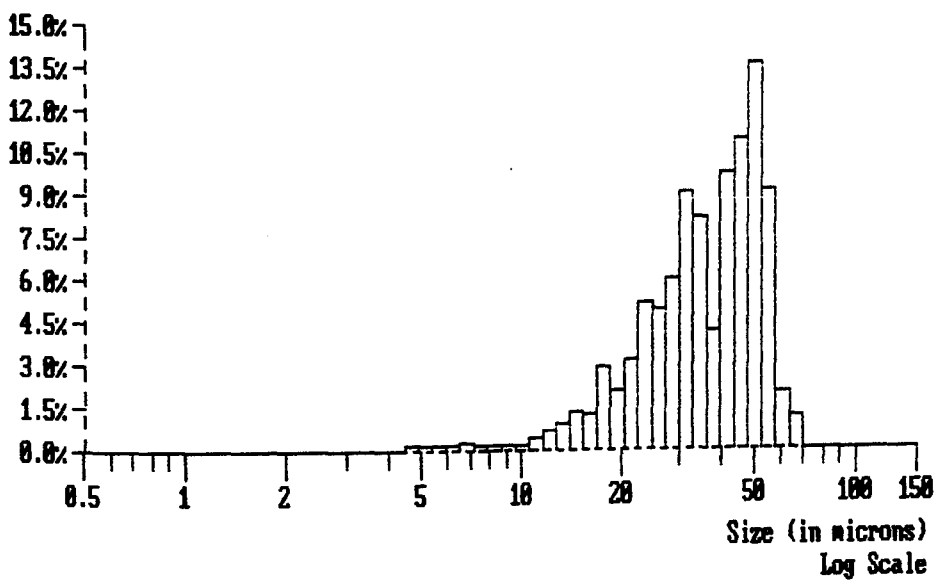


Fig 47 Droplet distribution of hydrophobic varnish
after stirring for 4 minutes at 70°C

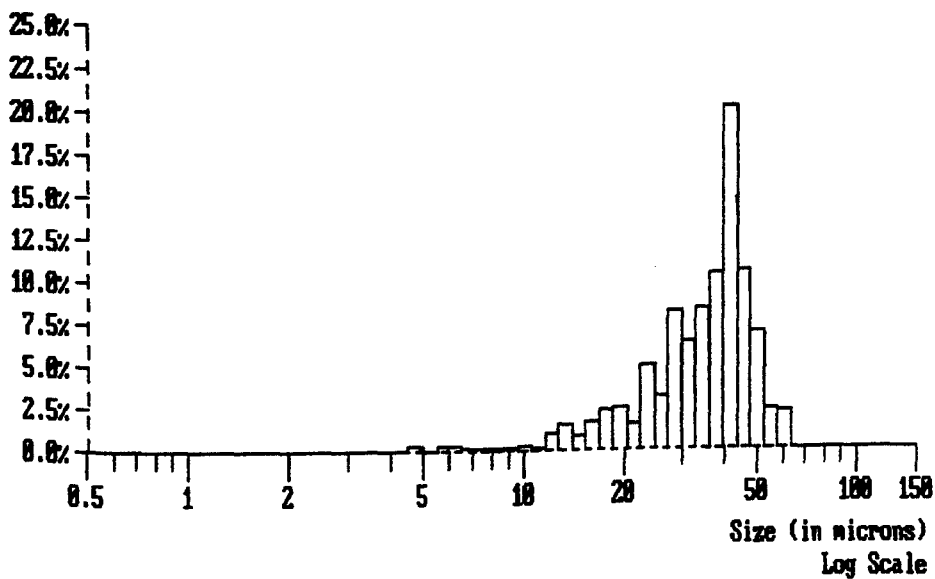


Fig 48 Droplet distribution of hydrophobic varnish
after stirring for 7 minutes at 70°C

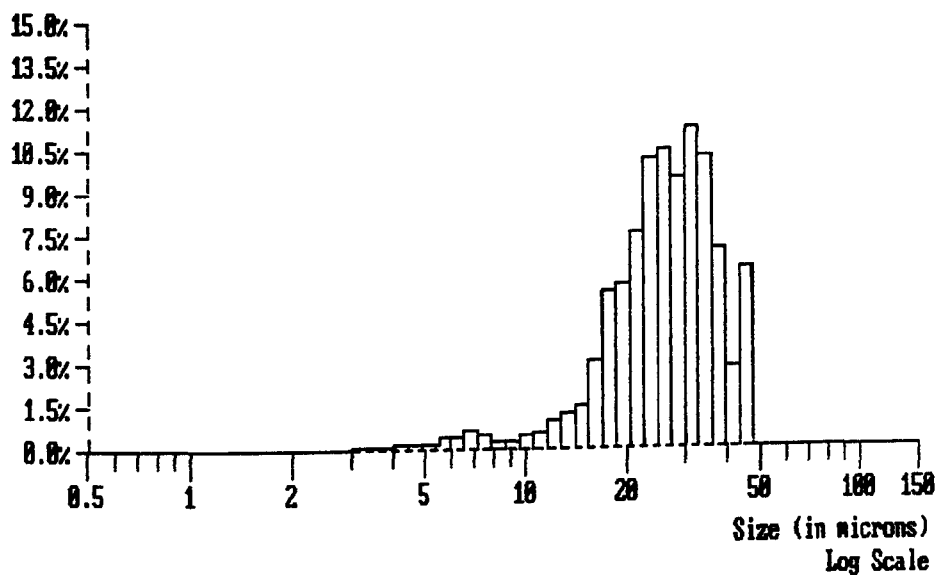


Fig 49 Droplet distribution of hydrophobic varnish
after stirring for 10 minutes at 70°C

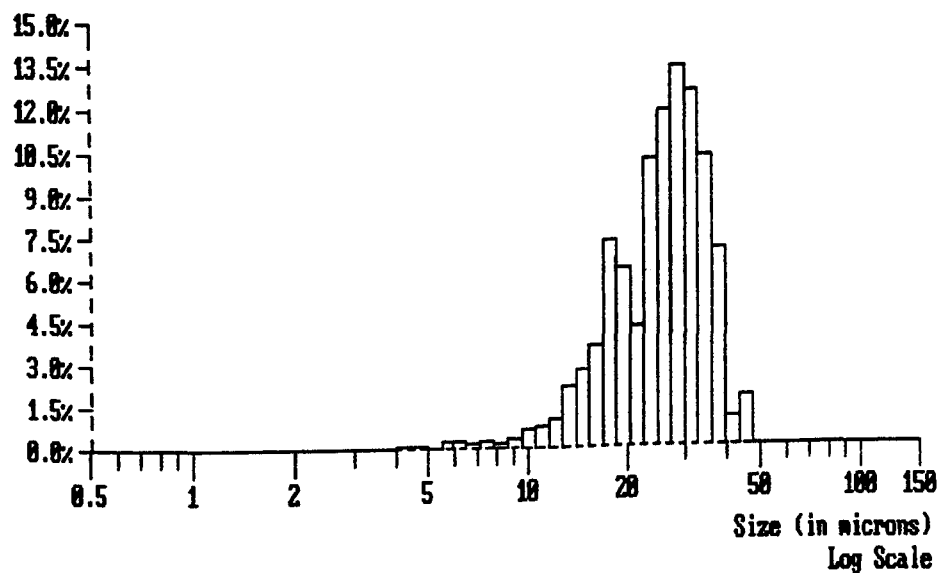


Fig 50 Droplet distribution of hydrophobic varnish
after stirring for 13 minutes at 70°C

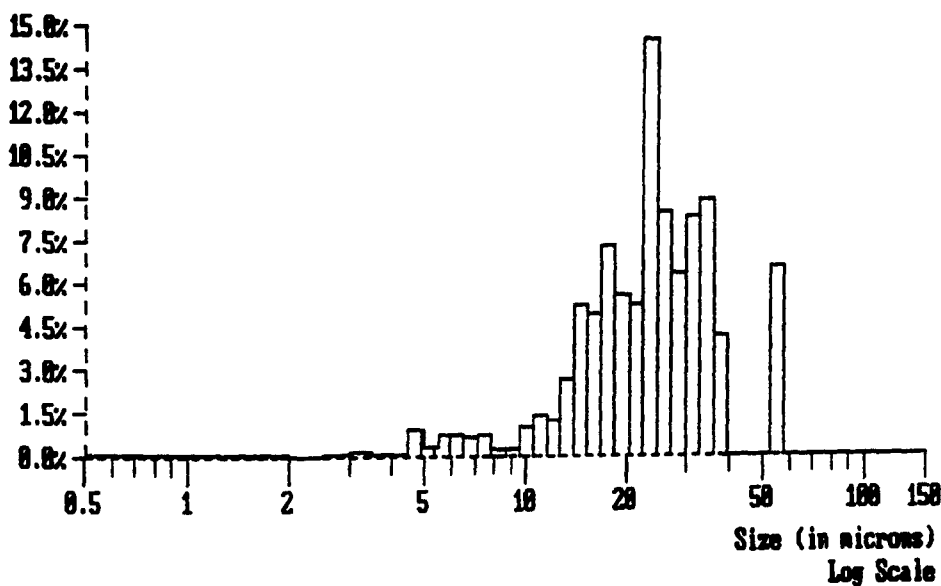


Fig 51 Droplet distribution of hydrophobic varnish
after stirring for 16 minutes at 70°C

At 40°C similar trends are seen with the mean droplet diameters of water dispersed within the hydrophilic varnish being generally smaller than those within the hydrophobic varnish (Fig 36). The breakdown of droplets within the hydrophilic varnish reaches a mean droplet diameter of ca. 5 microns after 5 minutes of stirring, compared with a mean droplet diameter of ca. 9 microns after 7 minutes of stirring in the hydrophobic varnish.

Comparing the droplet distributions of the hydrophilic varnish emulsion stirred at 40°C, it can be seen that, generally, the number of droplets above ca. 10 microns diminishes, whereas the number of droplets below 5 microns increases with increasing stirring time (Figs 52-56).

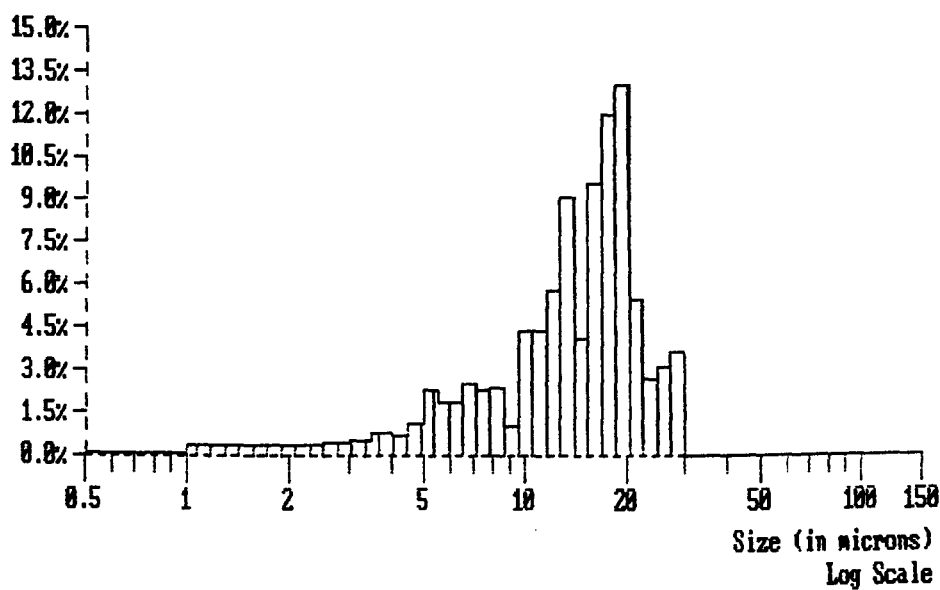


Fig 52 Droplet distribution of hydrophilic varnish
after stirring for 1 minute at 40°C

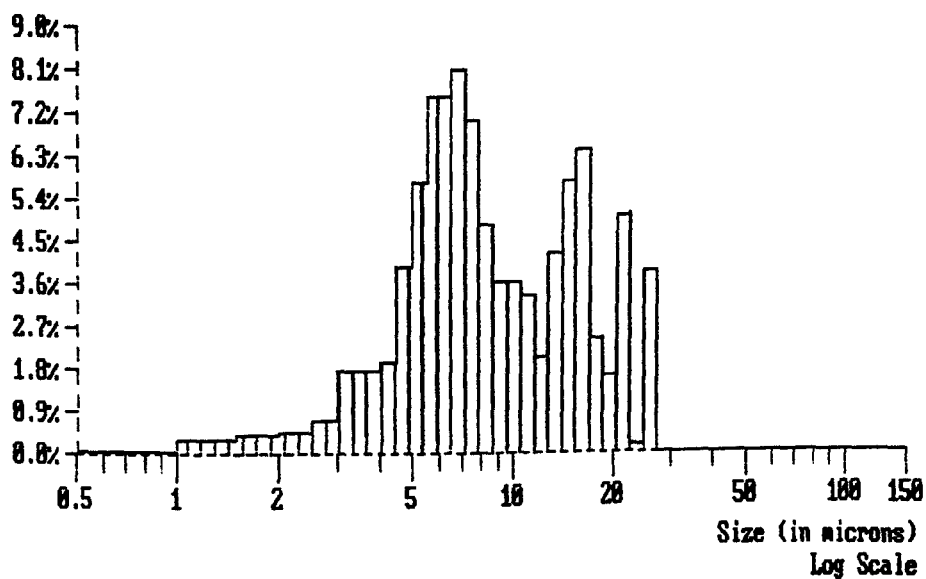
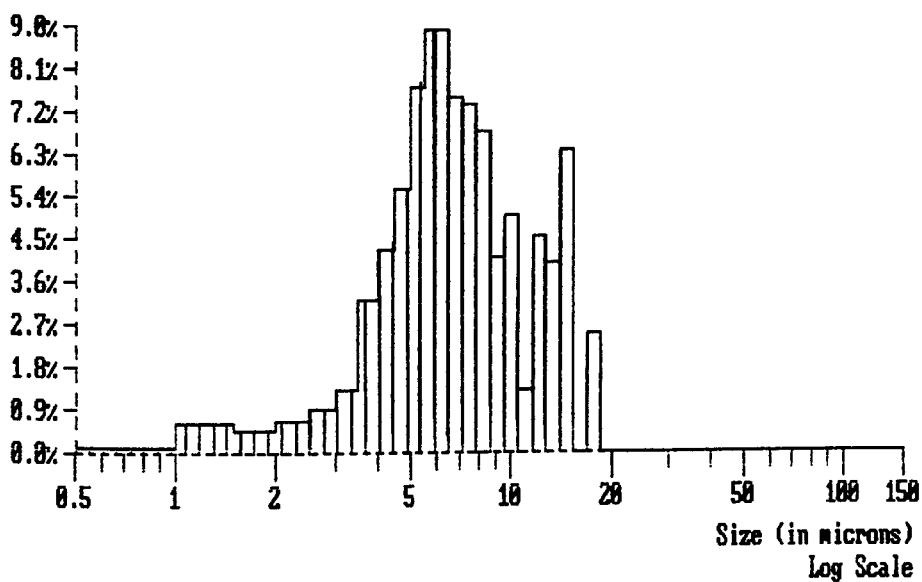


Fig 53 Droplet distribution of hydrophilic varnish
after stirring for 2 minutes at 40°C



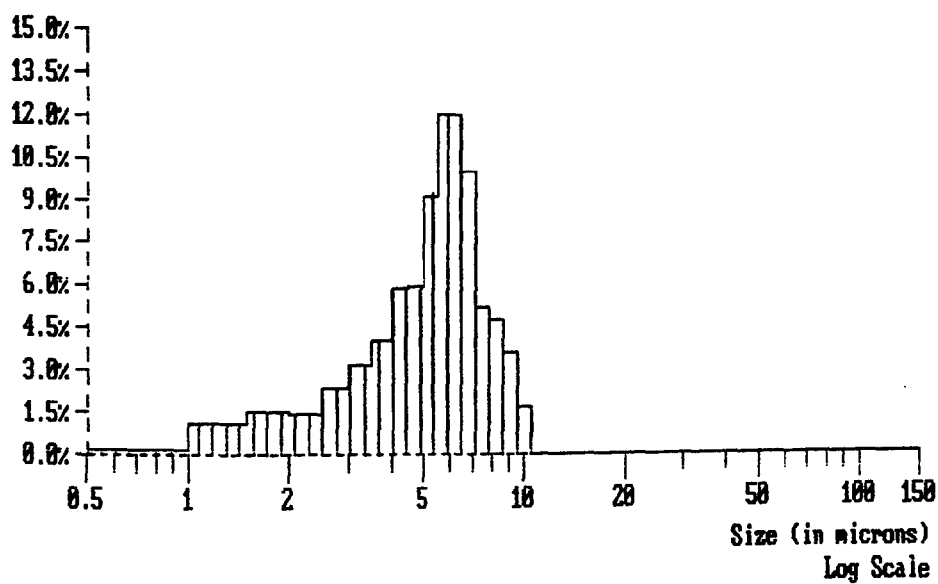


Fig 56 Droplet distribution of hydrophilic varnish
after stirring for 5 minutes at 40°C

Comparing the droplet distributions of the hydrophobic varnish emulsions at 40°C, it can be seen that, generally, the number of droplets above 20 microns diminish whereas the number of droplets below 10 microns increases with increasing stirring time (Fig 57-61).

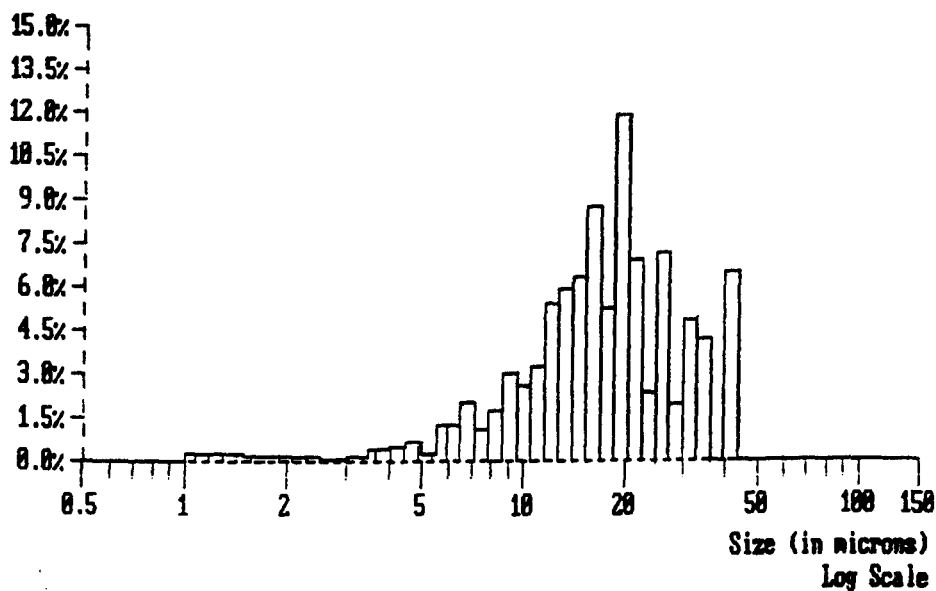


Fig.57 Droplet distribution of hydrophobic varnish
after stirring for 2 minutes at 40°C

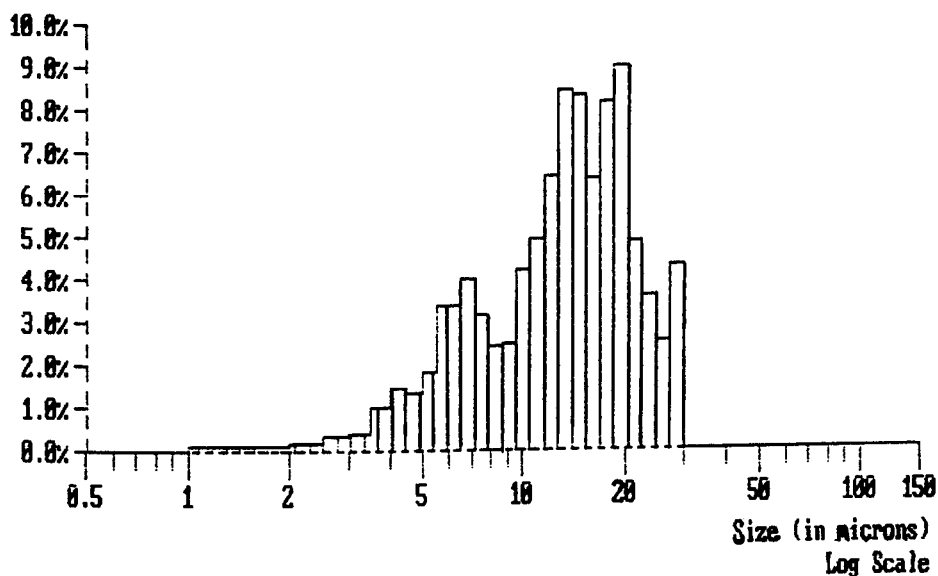


Fig 58 Droplet distribution of hydrophobic varnish
after stirring for 3 minutes at 40°C

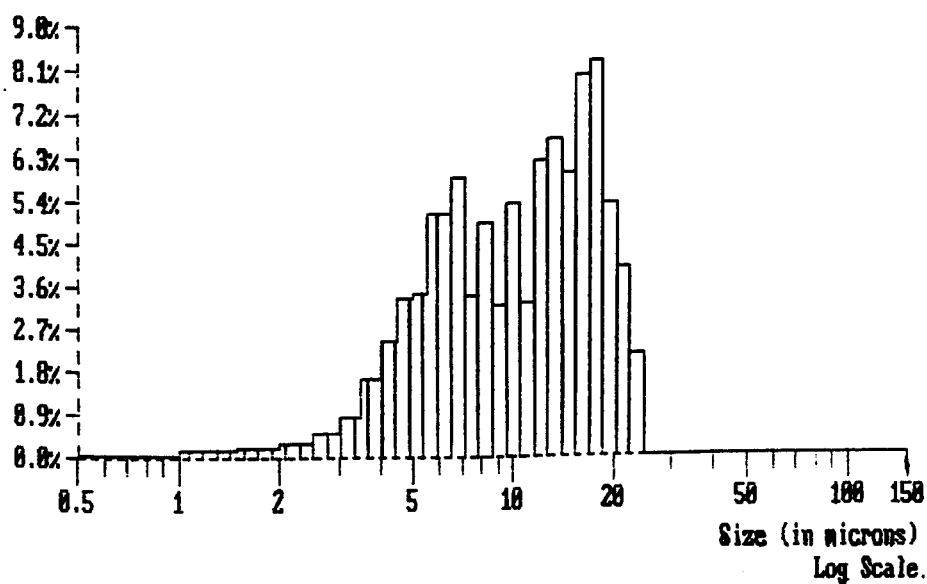


Fig 59 Droplet distribution of hydrophobic varnish
after stirring for 4 minutes at 40°C

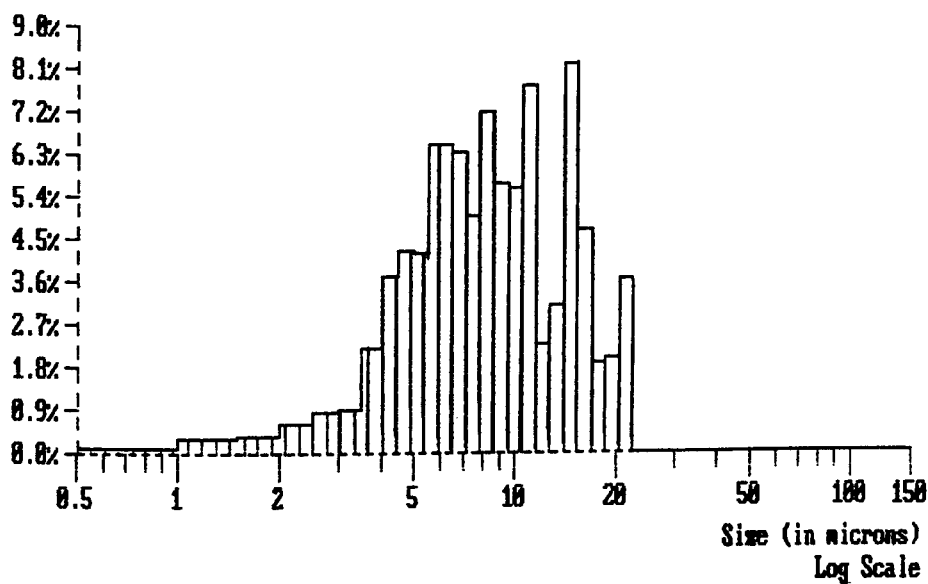


Fig 60 Droplet distribution of hydrophobic varnish
after stirring for 5 minutes at 40°C

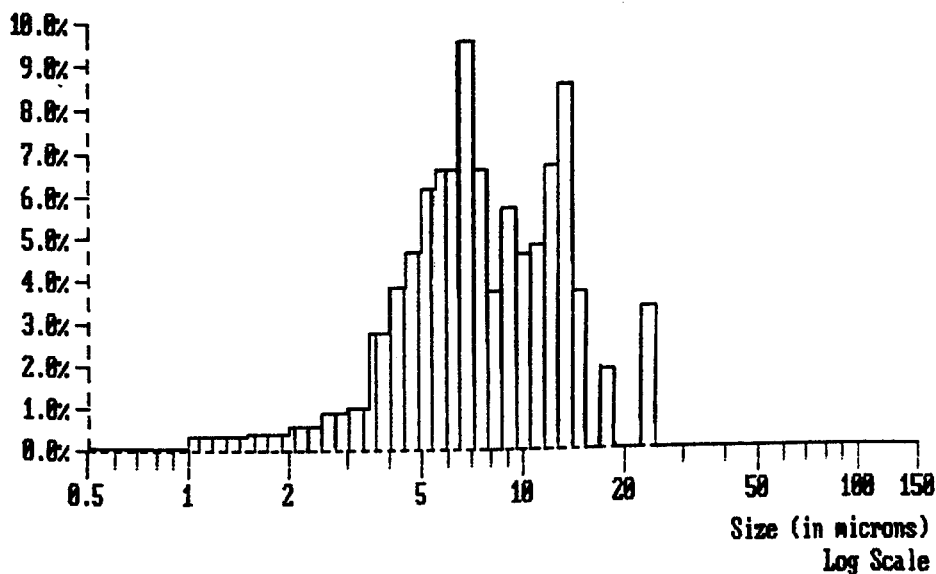


Fig 61 Droplet distribution of hydrophobic varnish
after stirring for 7 minutes at 40°C

In terms of colloid stability it may be inferred that the hydrophilic and hydrophobic varnish systems form metastable emulsions. Moreover, the smaller the size of the droplets in the disperse phase, the more stable the emulsion. Therefore, it may be concluded that the hydrophilic varnish system forms the more stable emulsions. These results are consistent with the greater shear stability of the fountain solution/hydrophilic varnish emulsions compared with the fountain solution/hydrophobic varnish emulsions (section 4.2.1).

4.3.2 Relationship of droplet breakdown to the square root of time

In order to simplify the data, an attempt was made to establish a linear relationship. It was found that there was at least an initial dependency upon the square root of time (Figs 62 and 63). This appears to coincide with the initial breakdown of the water droplets and is evident at both 70°C and 40°C. At 70°C the dependency upon the square root of time is apparent for the duration of the experiment. By comparison, for the water/hydrophobic varnish emulsion at 40°C there is a deviation from this dependency as the droplet size approaches a dynamic equilibrium. This raises the question of whether the process of droplet breakdown is controlled by different factors under different conditions; i.e. are the driving forces for the emulsification process different at 40°C and 70°C ?

The effects of temperature on the emulsification of the model varnish systems are discussed elsewhere (section 4.4).

These observations are reminiscent of the results of the Surland type studies where a dependence upon the square root of time was also found (section 4.4.1). There are various cases of relationships involving the square root of time to be found in literature concerning diffusion effects, for example, Fick's second law of diffusion⁵. However, given the magnitude of the time scales involved i.e. minutes, it is unlikely that these observations are due to the diffusion of surfactant moieties at the fountain solution/varnish

interface, as in the Marangoni effect, where the time scale would be of a lower magnitude.

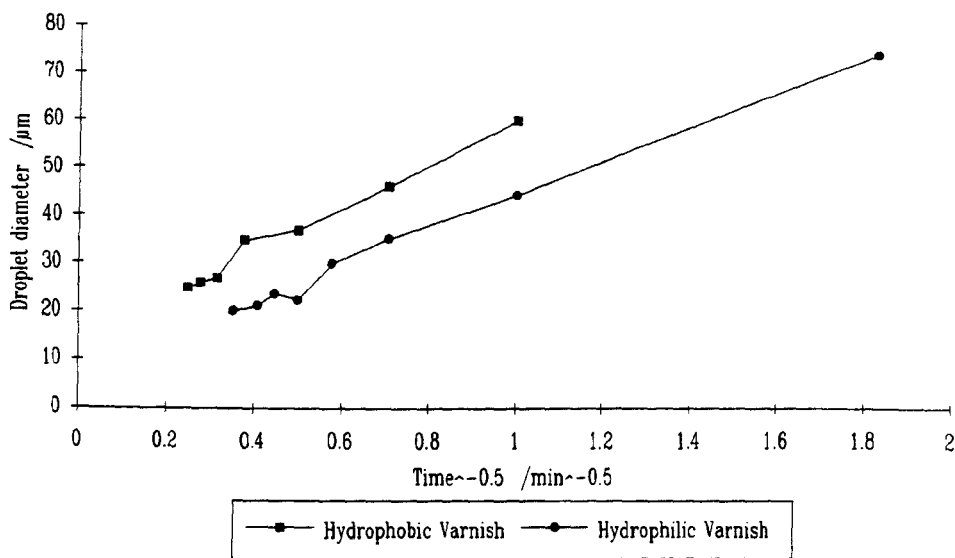


Fig 62 Relationship of emulsification of the model varnish systems to the square root of time at 70°C

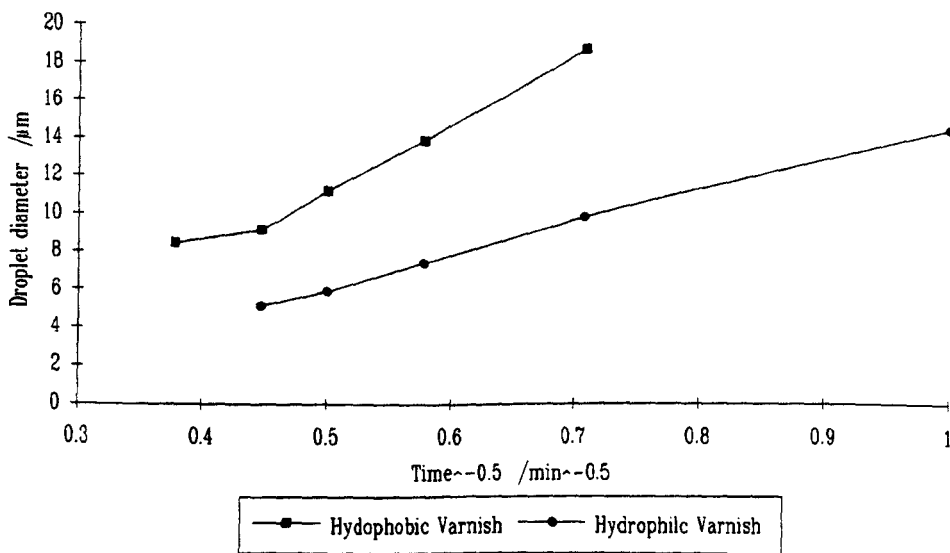


Fig 63 Relationship of emulsification of the model varnish systems to the square root of time at 40°C

4.3.3 Examination of the breakdown of water droplets in a lithographic heat-set varnish

Additional experiments concerning the extent of the breakdown of water droplets were carried out with a lithographic heat-set varnish (LTHS). This varnish, supplied by DSM Resins, was described as being a 'typical' formulation for a heat-set varnish. It is therefore useful to assess the performance of this varnish when subjected to the same tests as the other model varnishes. The emulsification of the LTHS varnish was conducted at 70°C and 40°C.

Overall, the trends observed in the experiments with the hydrophobic and hydrophilic varnishes were apparent in the LTHS varnish.

Comparing the breakdown of water droplets dispersed within the LTHS varnish at 70°C, it can be seen that the droplets produced are generally smaller than the hydrophobic and hydrophilic varnishes (Fig 64). However, the LTHS varnish and the hydrophilic varnish appear to follow a similar pattern of emulsification.

At 40°C the water droplets within the LTHS varnish are initially broken down at a faster rate than the hydrophilic and hydrophobic varnishes. After one minute of stirring the mean droplet diameters are similar at ca. 12 microns compared with ca. 14 microns for the hydrophilic varnish (a result for the hydrophobic varnish at one minute is not available). The final mean droplet diameter of the water droplets is similar to that of the hydrophilic varnish i.e. approximately 6 microns (Fig 65).

A dependency upon the square root of time was also apparent for the LTHS varnish at 70°C and 40°C (Figs 66 and 67); again showing a deviation as smaller droplets sizes are approached.

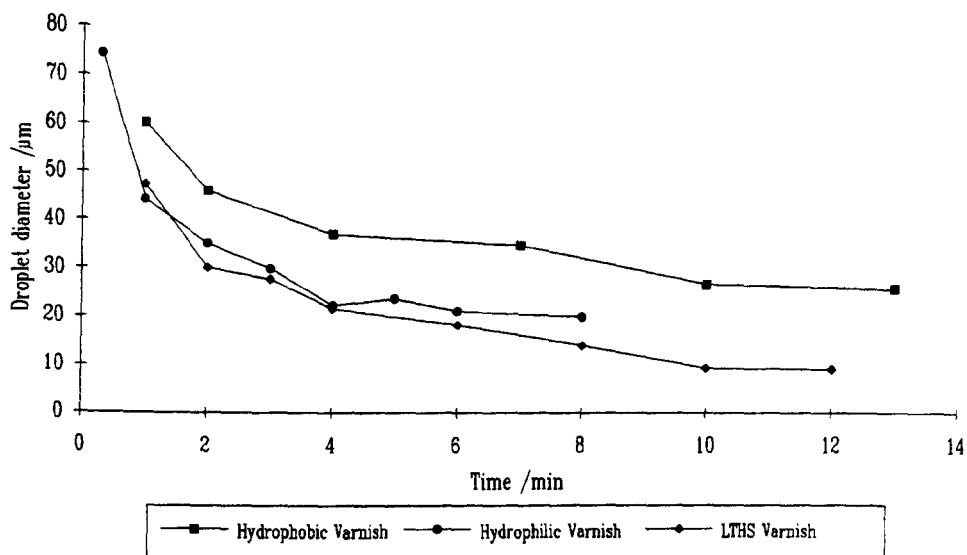


Fig 64 Comparison of the breakdown of droplets in the LTHS varnish with the model hydrophilic and hydrophobic varnishes at 70°C

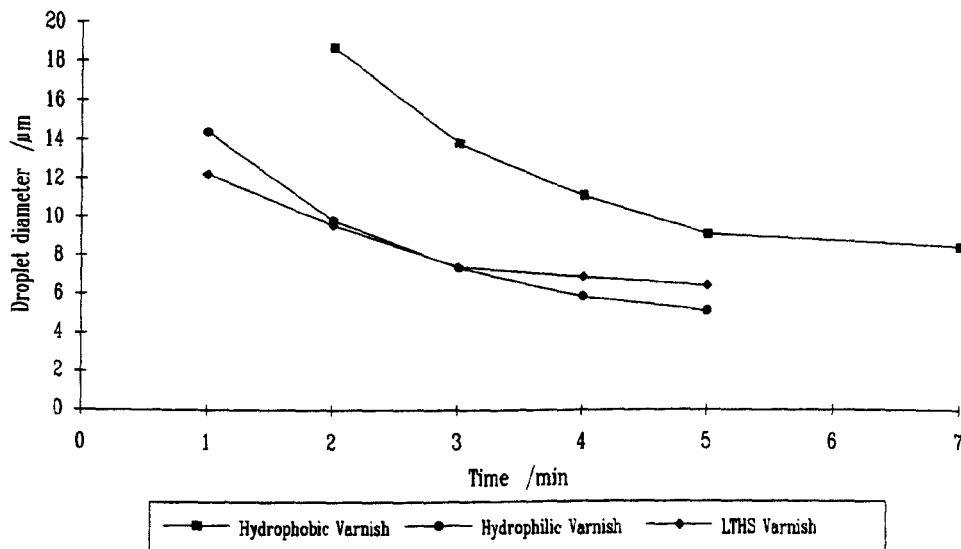


Fig 65 Comparison of the breakdown of droplets in the LTHS varnish with the model hydrophilic and hydrophobic varnishes at 40°C

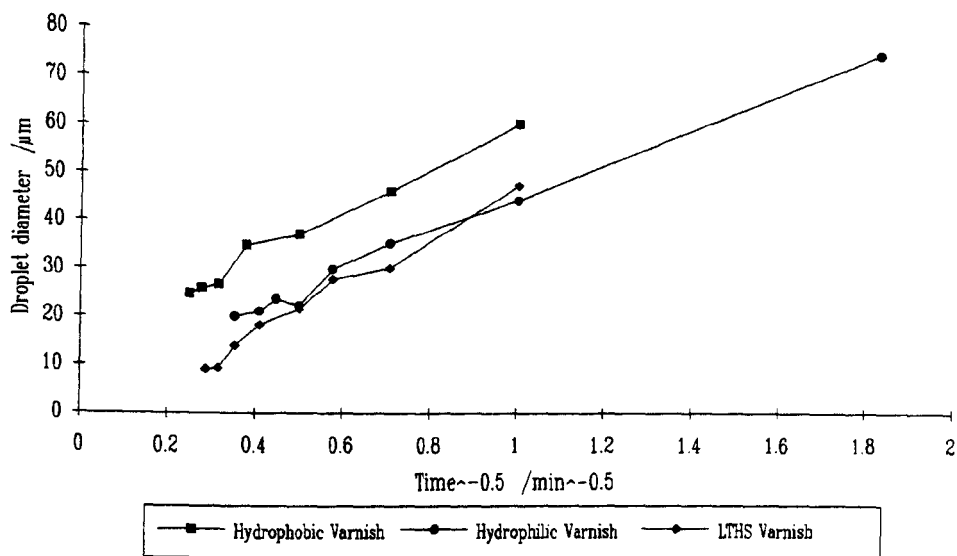


Fig 66 Relationship of the emulsification of the LTHS varnish with the square root of time at 70°C

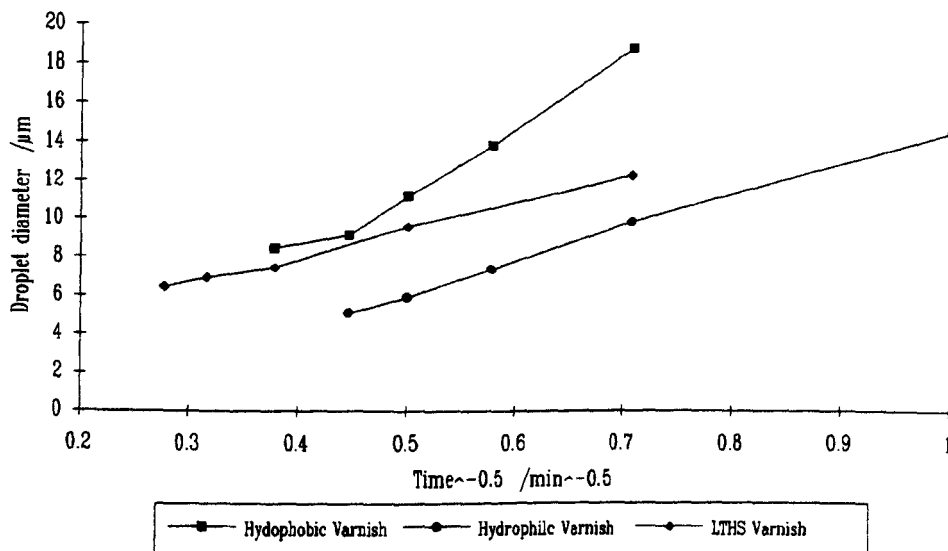


Fig 67 Relationship of the emulsification of the LTHS varnish with the square root of time at 40°C

4.4 Effects of temperature on emulsification

Comparing the emulsification studies on the hydrophobic varnish at 40°C and 70°C, it can be seen that the initial rate of droplet breakdown occurs faster and to a greater extent at the lower temperature (Fig 68).

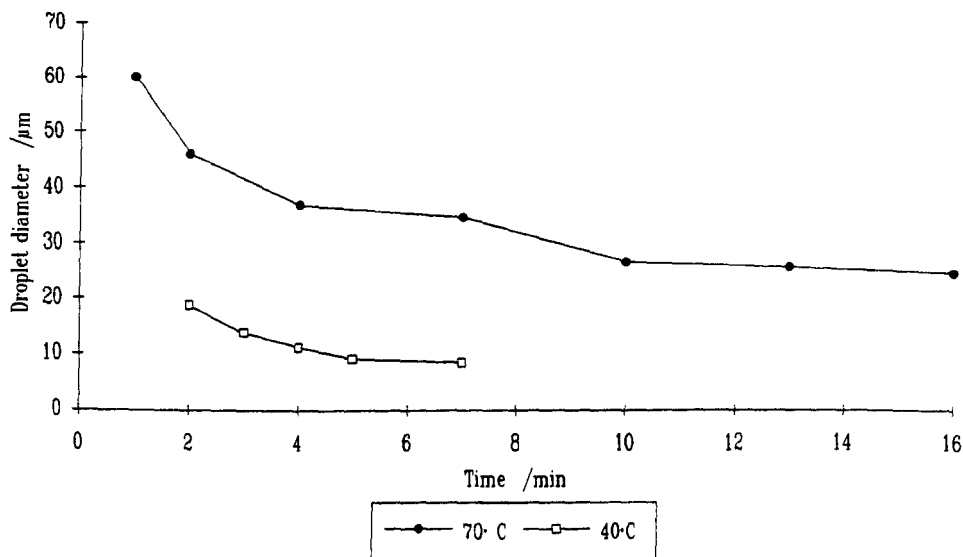


Fig 68 Breakdown of water droplets in the hydrophobic varnish at 40°C and 70°C

After 7 minutes of stirring at 40°C, the mean diameter of the water droplets was approximately 8 microns, compared with approximately 35 microns at 70°C.

Similar trends were apparent in the breakdown of water droplets in the hydrophilic varnish (Fig 69). After 5 minutes of stirring at 40°C, the mean droplet diameter was ca. 5 microns, whereas at 70°C the mean droplet diameter was ca. 25 microns.

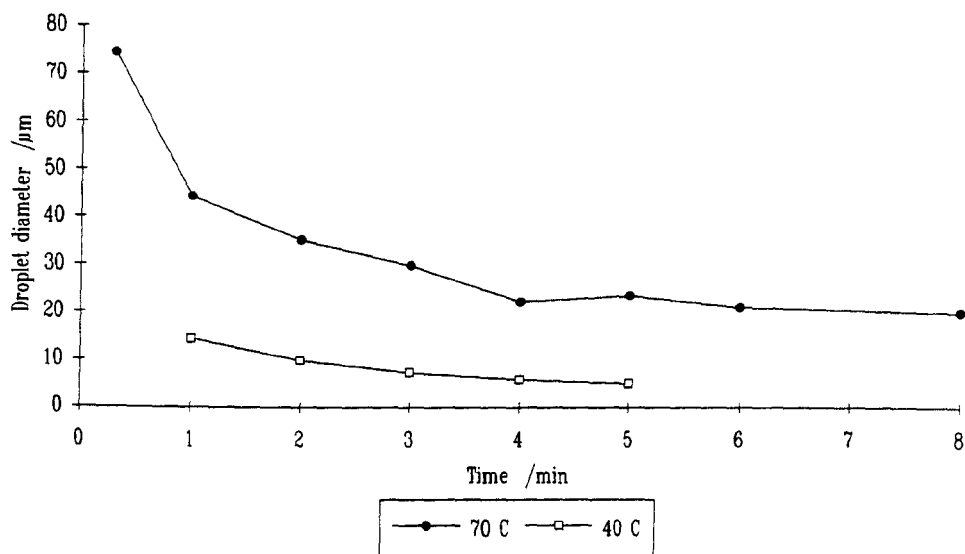


Fig 69 Breakdown of water droplets in the hydrophilic varnish at 40°C and 70°C

A similar trend was found in the emulsification of water into the LTHS varnish (Fig 70).

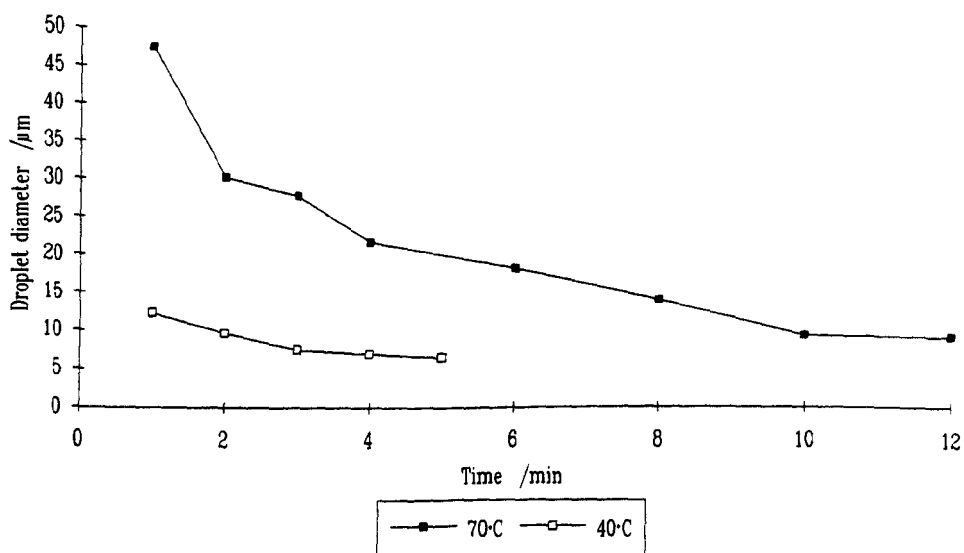


Fig 70 Breakdown of water droplets in the LTHS varnish at 40°C and 70°C

Given that the surface tension of most fluids decreases with increasing temperature, these observations seem surprising. A reduction in interfacial tension would increase the rate of emulsification. This is not the case with the model varnish systems.

There appears to be a lower limit upon the mean diameter attainable by the water droplets within each experiment; it is possible that a dynamic equilibrium has been reached. However, the fact that smaller droplets can be produced at 40°C would imply that the size of the droplets formed is determined by the local environment.

In order to explain these observations, it is necessary to examine the effect of temperature on other aspects of the emulsification process; the effect of temperature upon the viscosity of the model varnishes is of particular interest.

4.5 Determination of the effect of temperature on the viscosity of the model varnishes

Materials

Hydrophobic varnish

Hydrophilic varnish

Procedure

The Carri-Med CSL 100 rheometer was set up with a cone and plate geometry: cone diameter 2 cm; cone angle 1°.

Varnish (ca. 2 g) was placed on the rheometer, pre-sheared for 3 minutes at 2000 Pa and allowed to rest for 1 minute.

The rheometer was programmed to run at a constant stress of 1000 Pa, whereas the temperature was increased from 30°C to 70°C over a five-minute period.

The shear stress of 1000 Pa was selected to ensure that measurements would be taken across the specified temperature range. If the shear stress had been set too high, there was the possibility that the corresponding shear rates would go beyond the measuring capabilities of the rheometer if the viscosity of the varnish became very low.

A graph of viscosity against temperature was plotted.

Results

Comparing the viscosity of the varnishes, it can be seen that between 30°C and 50°C the hydrophilic varnish is more viscous than the hydrophobic varnish (Fig 71).

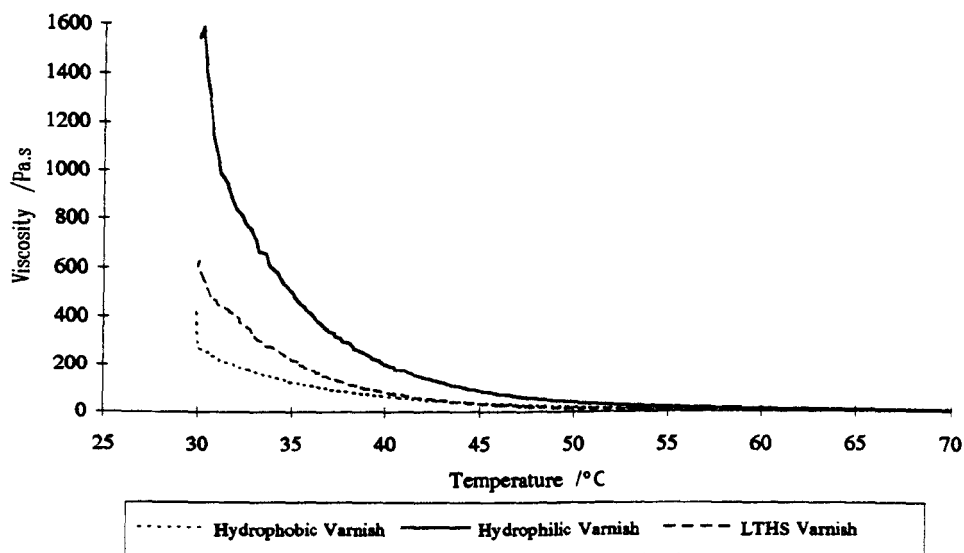


Fig 71 Effect of temperature on the viscosity of the model varnish systems

It can be seen that for all the model varnishes there is a decrease in viscosity as the temperature is increased from 30 to 40°C. However, above 50°C the viscosities of the model varnish systems are similar.

In the emulsification studies carried out at 40°C, the hydrophilic varnish was found to produce droplets that were generally smaller than those dispersed in the hydrophobic varnish. This raised the question as to whether the viscosity or the hydrophilicity of the varnish was responsible for these observations. Similar experiments, carried out at 70°C, where an essentially iso-viscous situation exists, should help to clarify this question. This will be discussed further in section 4.8.

4.6 Further effects of temperature on the size of the dispersed water droplets

This experiment was only performed with the hydrophilic varnish, due to the limited availability of the hydrophobic varnish.

Procedure

Varnish emulsions were prepared as previously described (section 4.3.1) at 35, 40, 45 and 50°C. Samples of the emulsions were tested on the Galai CIS-1 at one minute intervals.

The mean droplet diameters, determined after 5 minutes of stirring, were plotted against temperature. This time was selected because it represented the maximum mixing time of the emulsion formed at 35°C. After 5 minutes, this emulsion appeared to have reached a dynamic equilibrium, thus providing a suitable standard against which the other emulsions could be measured.

Results

It can be seen from Fig 72 that an increase in temperature leads to an increase in the mean diameter of the water droplets.

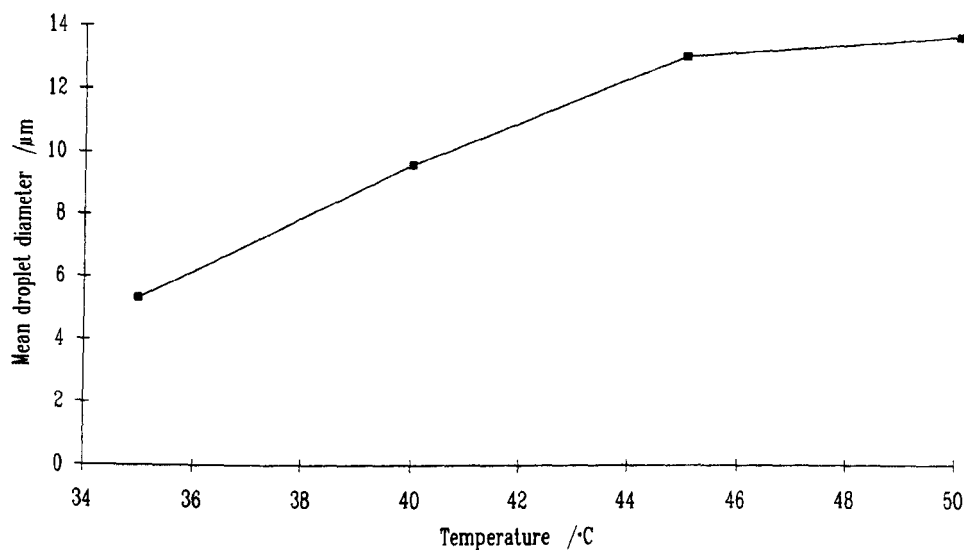


Fig 72 Mean droplet diameter v temperature where $t = 5$ minutes

4.7 Determination of the effects of temperature on the interfacial tension between water and the model varnish systems

The interfacial tension between water and the model varnish systems was measured according to the procedure given in section 3.9.

Measurements were carried out at room temperature (i.e. 19-21°C) and then at 25, 30, 35, 40, 50, 60 and 70°C. The interfacial tension average from three measurements was plotted against temperature.

Results

The results show that the interfacial tension at the water/hydrophobic varnish interface is higher than that at the water/hydrophilic varnish interface (Fig 73). The interfacial tension of the water/LTHS varnish system is similar to that of the hydrophilic varnish system across the temperature range measured.

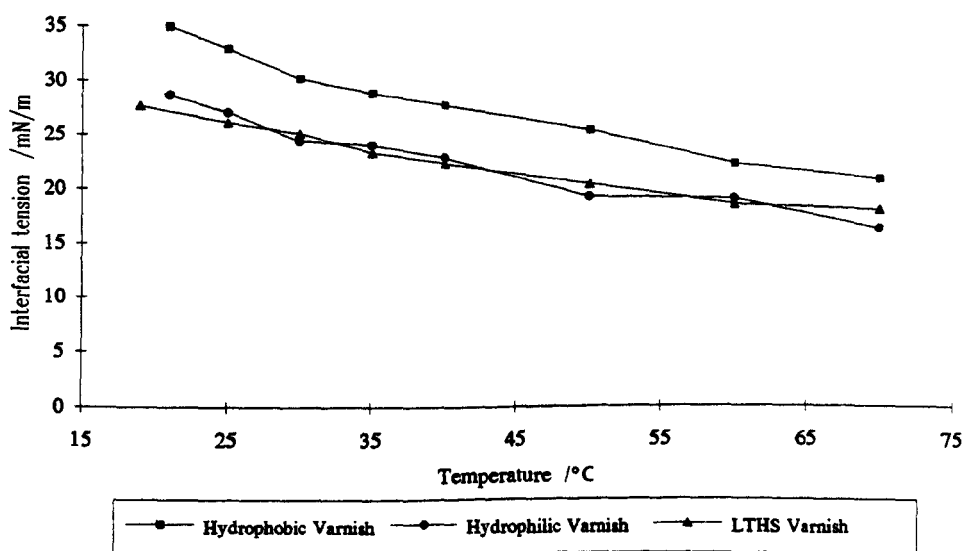


Fig 73 Interfacial tension v temperature for the model varnish systems

Additionally, it was found that the interfacial tension within all the varnish systems decreased with increasing temperature. However, the change in interfacial tension is relatively small, with a decrease of ca. 6 mNm^{-1} being recorded in each case over the temperature range measured i.e. $40\text{-}70^\circ\text{C}$. The behaviour of all the varnish systems is characteristic of most fluid materials in that the interfacial tension decreases with increasing temperature.

It might be expected that a reduction in the interfacial tension would lead to emulsions being formed at a faster rate, with a smaller mean particle size distribution and consequently increased stability. It is known that if the interfacial tension between two fluids is sufficiently low, emulsification can take place virtually instantaneously³. If the particles or droplets produced are small enough to be thermodynamically as well as colloiddally stable, then the emulsion should remain stable. This is not the case in the model varnish systems.

For the model varnish systems, increasing the temperature at which the emulsion was formed reduces the rate of and extent of droplet breakdown. Given these observations, it can be concluded that the interfacial tension at the water/varnish interface is not the main factor in the breakdown of water droplets within the model varnish systems.

However, interfacial tension is an important factor in the colloidal stability of emulsions; lower interfacial tensions can enhance emulsion stability^{3,4} whereas higher interfacial tensions will reduce emulsion stability. It is possible that the role of interfacial tension in the emulsification of these varnish systems is connected with the stability of the emulsions. This statement is supported by the results from the rheological studies (section 4.2.1) where it was found that the emulsions formed with the hydrophobic varnish and hydrophobic ink were less stable than their hydrophilic counterparts.

4.8 Discussion

Several studies have been carried out investigating the deformation and breakdown of droplets within a shear field⁵⁶⁻⁶⁰. Stamatoudis and Tavlirides studied liquid-liquid dispersions in which there was a difference in the viscosities of the continuous phase and the disperse phase⁶¹. The breakdown of droplets was studied as the systems were agitated. These systems exist in a dynamic state where droplets are constantly being broken down as well as coalescing. A model for droplet size distribution which follows a population balance equation for all droplets of volume v was proposed:

$$\int_v^L \tau_b(v')' \nu(v) \beta(v', v) dv' + \int_0^{v/2} F(v - v', v') dv' = \tau_b(v) + \int_0^L F(v, v') dv' + d[N(t)A(v)]/dt \quad (18)$$

where $\tau_b(v)$ is the number of droplets of size v breaking per unit volume of dispersion per unit time; $F(v, v')dv'$ is the number of pairs of droplets of size v and v' coalescing per unit volume of dispersion per unit time; $\nu(v)$ is the number of daughter particles resulting from the breakage of a droplet of volume v' ; $\beta(v', v) dv'$ is the fraction of droplets with volume v formed by the breakage of droplets of volume v' ; $A(v)$ is the volume fraction of droplets of size v ; $N(t)$ is the number of drops of all sizes per unit volume at time t ; and L is the maximum drop size present in the dispersion. The first term on the left-hand side of the equation represents the contribution of drops of volume v formed through the breakdown of larger drops whereas the second term represents the coalescence of the smaller drops. The first two terms on the right hand side represent the loss of drops of size v due to the breakdown of droplets, whereas the last term is the accumulation term.

According to this model, for breakdown of a droplet to occur, it is necessary to supply sufficient energy to the droplet in order to overcome the force that holds it together. This force will be a function of the surface tension of the droplet. The energy for the

breakdown will come from the immediate environment of the droplet, either as kinetic energy resulting from turbulent flow, shear mechanical forces resulting from shear or as a combination of the two.

The rate at which droplets are broken down depends on the interfacial tension and the hydrodynamic field surrounding the droplet. The dispersion of systems where the viscosity of the continuous phase is relatively low, is dominated by flow. However, as the viscosity of the continuous phase increases, the influence of turbulent flow is diminished and the breakdown of droplets is dominated by shear forces which become more important⁶¹.

In the present study it was found that the rate and extent of the breakdown of water droplets differed according to the viscosity of the varnish in all the model varnish systems. For example, for the hydrophilic varnish at 70°C (where the viscosity was 5 Pas), the mean droplet diameter was ca. 20 μm . However, at 40°C (where the viscosity was 300 Pas), the mean droplet diameter was ca. 5 μm . These results are in agreement with observations made by Flumerfelt where droplets subjected to a specific set of shear parameters would reach a minimum size⁶².

The observations made in the present study may be clarified by comparing the shear stress against shear rate curves for the hydrophilic varnish at 70°C and 40°C (Fig 74). It can be seen that whereas the shear rates in the hydrophilic varnish at 70°C may be considerably greater than those at 40°C, the corresponding shear stresses are lower at 70°C. Thus, at 40°C the shear stress rises rapidly to $> 4000 \text{ Pa}$ at shear rates of ca. 50 s^{-1} ; whereas, at 70°C the shear stress lies below 3000 Pa at 2500 s^{-1} . Given that the shear forces dominate the breakdown of droplets in systems where the continuous phase has a high viscosity, these results confirm that viscosity plays a major role in the breakdown of droplets in the water/varnish systems.

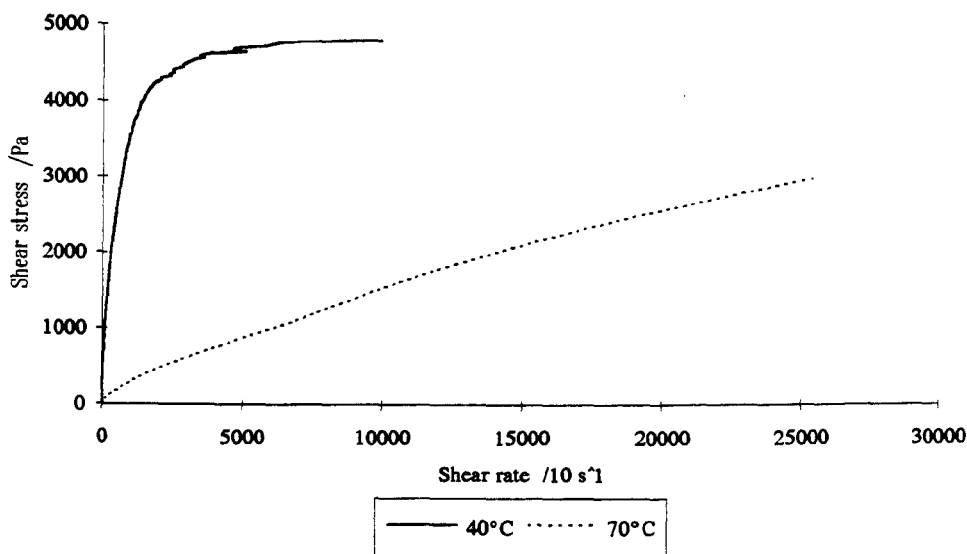


Fig 74 Shear stress v shear rate curves for the hydrophilic varnish at 40°C and 70°C

The emulsification process is essentially a combination of two processes: i.e. droplet breakdown accompanied by coalescence or demulsification. The rate of coalescence is influenced by several factors. One factor is the rate of collision of the dispersed droplets, which occurs as a function of droplet size and the hydrodynamic environment of the dispersion system. Another factor that can influence the rate of coalescence is the coalescence efficiency between colliding droplets. This is governed by the time that two colliding droplets remain in contact with each other and the time required for the film of continuous phase to drain away. This film must be removed in order for the surface of the droplets to rupture, thereby allowing coalescence to take place. For systems where the viscosity of the continuous phase is higher, a lower rate of film drainage is expected thus leading to a lower rate of coalescence.

The fountain solution/varnish emulsions investigated in this study are systems in which the continuous phase has a high viscosity relative to that of the disperse phase. The observations made with regard to this work appear to be consistent with those made by Stamatoudis and Tavlarides⁶¹.

Where the viscosity of the varnish systems was high i.e. at a temperature of 40°C, the apparent rate of droplet breakdown was greater than that of the varnish system at a lower viscosity i.e. 70°C. Additionally, the rate of coalescence is hindered by the relatively high viscosity of the varnish.

Thus, where the viscosity of the system was reduced at 70°C, the apparent rate of droplet breakdown was lower and the resulting droplet mean diameters higher than those at 40°C.

Under the conditions of these experiments, the speed of the Moulinex blender was set at 900 rpm, but this stirrer does not necessarily operate at a constant speed. In reality, the stirrer will be influenced by the rheology of the materials being stirred. In this case in a low viscosity medium, the rotational speed would approach 900 rpm, while at high viscosity the rotational speed of the stirrer would be comparatively slower.

The increase in rotational speed available to the lower viscosity system provides a greater opportunity for collisions to take place. The lower viscosity will also lead to improved film drainage.

Whereas the above offers an explanation for the observations made in the model varnish systems and highlights the role of viscosity in the emulsification process, the question of how the hydrophobicity of the model materials affects the emulsification process still remains. Rosted and Medson⁶⁵ reported that initially the amount of emulsified water is affected by the viscosity of the ink; however, the water/ink interfacial tension will govern the relative amount of surface water that can be released.

The experiments show that irrespective of temperature, the extent of droplet breakdown in the hydrophobic varnish is less than that of the hydrophilic varnish. In addition to this, the interfacial tension at the fountain solution/hydrophobic varnish is higher in comparison with the hydrophilic varnish.

In order to address this question, consider the formation of the hydrophobic and hydrophilic varnish emulsions at 70°C. It has previously been shown that above 50°C the viscosities of both materials are comparable, therefore at 70°C the effects of viscosity are minimised.

Assuming that the breakdown of water droplets is at the point where their surface areas are identical in each varnish system, if two droplets of water were to coalesce the following situation might occur:

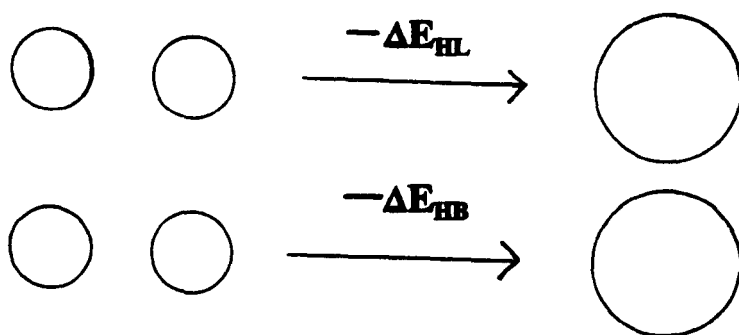


Fig 75 Coalescence of two droplets of equal surface area

where HB refers to the hydrophobic system and HL refers to the hydrophilic system.

Coalescence of the droplets would lead to a reduction in the interfacial area resulting in a loss of surface free energy: i.e. $-\Delta E_{HL}$ for the hydrophilic system and $-\Delta E_{HB}$ for the hydrophobic system.

At 70°C the interfacial tension of the water/varnish interface is higher in the hydrophobic varnish system than in the hydrophilic varnish system. Given that these systems have not been stabilised by external means (i.e. by surface active materials), the driving force for coalescence should come from the interfacial energy. It would therefore be expected that the rate of coalescence of the water droplets within the hydrophobic varnish would be faster than that of droplets in the hydrophilic varnish.

This could be incorporated into a simple Arrhenius law

$$\text{Rate} \propto e^{-\Delta E/RT} \quad (19)$$

where $R = 8.31 \text{ kJmol}^{-1}$, $T = \text{temperature /K}$.

According to the above expression, if ΔE_{HB} is larger than ΔE_{HL} it would be expected that the rate of coalescence of water droplets would be higher for the hydrophobic varnish. This provides a possible explanation for the results obtained here.

5 Studies of emulsions prepared under high shear rate conditions

In order to establish the optimum conditions for producing emulsions with the high speed disperser, it was necessary to carry out preliminary studies. The stirring speed for the varnish was optimised at 9000 rpm. At this speed the stirring pattern of the varnish was found to have a 'doughnut' configuration which is said to provide the optimum flow patterns for efficient mixing⁴⁸. The peripheral speed of the 2.5 cm impeller at 9000 rpm is ca. 12 ms^{-1} which is similar to the running speed of a sheet-fed press².

A sample of varnish (30 g) was weighed into the double-walled stainless steel beaker. The beaker was clamped in place in the Dispermat and a thermocouple was attached to the stationary outer shaft of the stirrer so that the end of it was immersed below the surface of the varnish and towards the wall of the beaker. The varnish was stirred at 9000 rpm and within 35 seconds the temperature increased from 21°C to 60°C .

This rapid increase in temperature arises as a result of the mechanical energy involved in stirring a high viscosity medium that is being dissipated as heat. Although this illustrates the variability of temperature during high shear rate stirring, it also demonstrates the difficulty of controlling the experimental conditions. It has already been shown within these studies that temperature affects the droplet size distribution of the emulsion formed; therefore it is necessary to limit such temperature changes. This will be achieved by diluting a previous batch of hydrophilic varnish with a petroleum distillate (i.e. a 1:1 mixture of PKWF 6/9 and PKWF 6/9 AFN) until suitable temperature conditions are attained.

5.1 Determination of the dilution required to stir the varnish under high shear rate conditions

Procedure

Hydrophilic varnish (45 g) was weighed into a glass beaker which was then placed on a hot plate and heated to 80°C. The petroleum distillate mixture (5 g) was stirred into the varnish to give a 90% (w/w) varnish mixture. The mixture was heated for a further 2 minutes, removed from the heat and allowed to cool to room temperature.

The diluted hydrophilic varnish (30 g) was weighed into the double-walled stainless steel beaker. The beaker was set up as described previously (section 5). The varnish was stirred at 9000 rpm and the temperature was monitored over 5 minutes with readings being taken at 30-second intervals.

This procedure was repeated for the hydrophilic varnish diluted to concentrations of 85% and 80% (w/w).

A graph of temperature against time for each dilution was plotted.

Results

Comparing the results, it can be seen that the 80% varnish mixture approaches a relatively constant temperature after 2 minutes of stirring, with an increase of 2°C in the final 3 minutes of stirring to give a final temperature of 45°C (Fig 76). The 85% and 90% mixtures gave higher end temperatures (i.e. 53°C and 57°C respectively) which was to be expected.

It was decided that the 80% varnish mixture provided a more controllable mixture, with regard to temperature changes, for the high shear rate experiments. The 85% varnish mixture did not reach a steady temperature during the test and was considered to be

unsuitable. Therefore, all subsequent experiments under the high shear rate conditions will be carried out with an 80% varnish mixture (w/w).

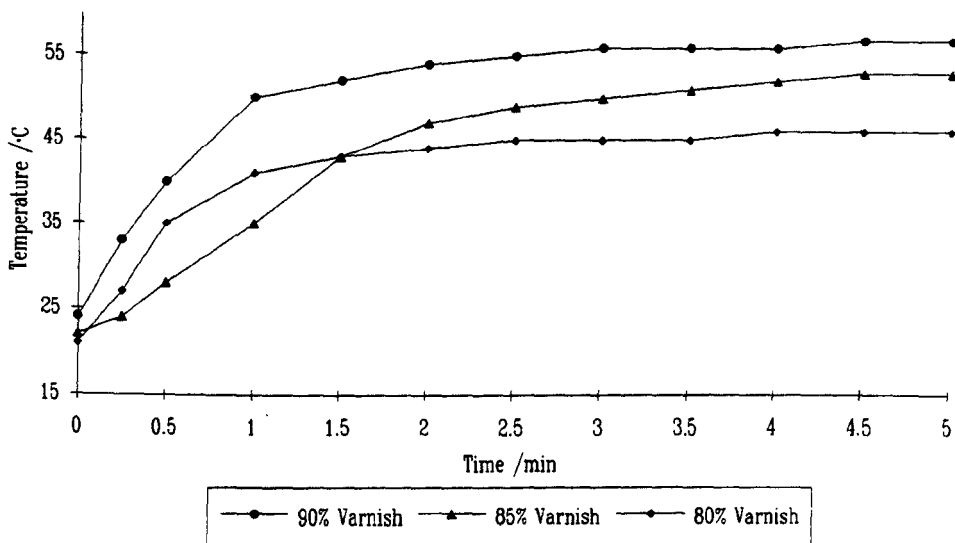


Fig 76 Temperature v stirring time curves for the hydrophilic varnish diluted to 80%, 85% and 90% concentration

5.2 Characterisation of a new batch of hydrophilic varnish

A new batch of varnish was prepared as detailed in section 3.2. This enabled all the remaining experiments to be carried out on the same basic varnish so that valid comparisons could be made. In order to establish how this batch of varnish responded to the stirring conditions of the Dispermat, the procedure adopted in section 5.1 was repeated on the new varnish. The varnish was diluted to 80% with a 1:1 mixture of PKWF 6/9 and PKWF 6/9 AFN. The varnish mixture (30 g) was stirred at 9000 rpm for 5 minutes and the temperature changes recorded. The diluted varnish was allowed to cool to room temperature before stirring for a further 5 minutes. This sequence was repeated again. At least 1 hour had elapsed between each run.

Results

The new batch of hydrophilic varnish responds in a similar fashion to the previous batch of varnish (Fig 77). This experiment shows that the stirring action of the Dispermat provides constant conditions in terms of energy input and subsequent heat generation. This means that any temperature changes experienced during the mixing of the varnish or emulsion (under these conditions) should be constant throughout. It is clear from these runs - which have a variation of $\pm 1^{\circ}\text{C}$ - that repeated stirring does not significantly affect the way in which the varnish responds. The high level of reproducibility of the experimental conditions using the Dispermat is important in that the heat content increase, which will depend on viscosity and stirring speed, is reproduced reliably. This is of particular relevance for some of the experimental work that follows.

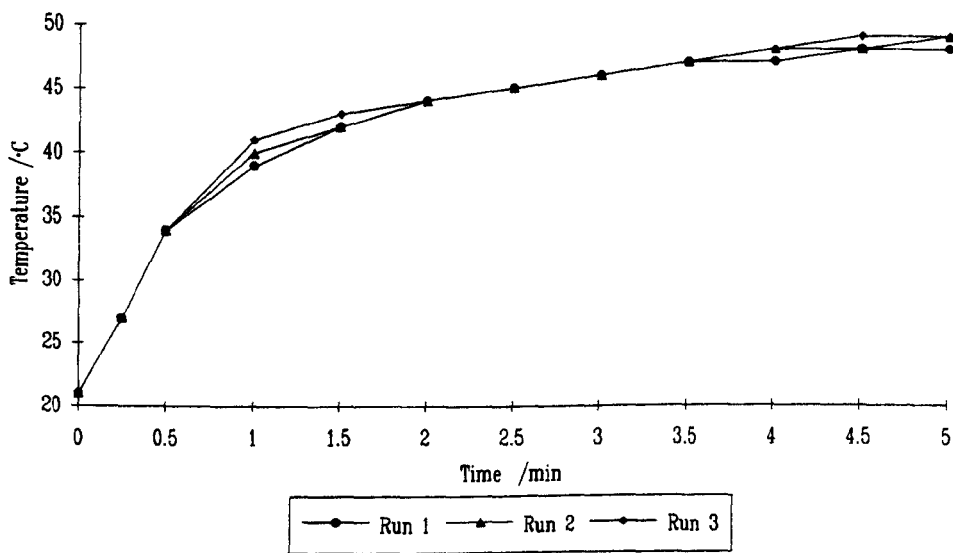


Fig 77 Temperature v stirring time curves for the hydrophilic varnish

5.3 Effects of temperature changes on the emulsification of a model

varnish system

During the printing process, temperature changes - in either direction - occur for several reasons. For example, the heat generated as the ink is distributed throughout the inking rollers may be counteracted by the addition of fountain solution to the plate or the ink which reduces the temperature⁶⁶.

It was found that a change in temperature which was accompanied by a change in viscosity affects the way in which the fountain solution droplets are broken down (sections 4.4, 4.5 and 4.6). At higher temperatures (and lower viscosity) dispersion of demineralised water under low shear conditions produced larger droplets; whereas at lower temperatures (and higher viscosity) the demineralised water is dispersed more finely.

It may be inferred that changes in temperature would also affect the interaction between the model varnishes and the water under high shear conditions. Similarly, in a press situation the question arises as to whether temperature variations will affect the ink/water balance.

The following experiment is designed to examine how the distribution of droplets within the demineralised water/varnish emulsion responds to changes in temperature. The emulsion is subjected to increases and reductions in temperature in the range of 30-50°C to enable comparisons to be made with the previous work carried out under low shear rate conditions.

5.3.1 Determination of the effects of temperature changes on the emulsion of a model varnish system under high shear rate conditions

Materials

Hydrophilic varnish

Demineralised water

Procedure

The diluted 80% hydrophilic varnish (30 g) was weighed into the double-walled stainless steel beaker. The beaker was clamped in the Dispermat disperser and a thermocouple was fastened to the stationary outer shaft of the stirrer with its tip immersed in the varnish (as described in section 5).

The varnish was stirred, without cooling, at 9000 rpm until a constant temperature of 41°C was reached (i.e. after 5 minutes).

Demineralised water (6 g) was then dribbled into the vortex of the varnish over a 20 second period and the stirring continued for 5 one-minute periods. The mixture was allowed to rest for 1 minute between each period of stirring. The inclusion of the 'rest periods' was based on observations made during the development of the Surland test which showed that the emulsification of water/ink systems was more efficient when shearing was applied in a stepwise fashion^{32,33}.

After stirring for a total of 5 minutes, a sample of the emulsion was removed and tested on the Galai CIS-1. The emulsion was stirred for a further three 1-minute periods until the distribution of the droplets in the emulsion appeared to reach a dynamic equilibrium.

Water was circulated around the double-walled vessel at 40°C. When the temperature of the emulsion had reached 40°C the droplet distribution was measured. The emulsion was

stirred for 1 minute (during which the temperature of the emulsion increased from 40°C to 43°C) before a sample was removed and examined on the Galai CIS-1.

The emulsion was heated to 50°C (using the water jacket) and stirred for 1 minute before the droplet distribution was measured. The temperature of the emulsion remained constant at 50°C.

The same emulsion was cooled to 30°C (by circulating the water at just below 30°C) and sampled before stirring for 1 minute and again afterwards. During the stirring there was a temperature change from 30°C to 36°C.

This procedure was repeated at 45°C and 50°C with the temperature of the emulsion remaining constant ($\pm 1^\circ\text{C}$) at these temperatures during stirring.

Results

The effect of changing temperature on the mean droplet diameter of the dispersed water droplets is shown in Table 9.

Temperature °C	Mean droplet diameter μm
40	1.42
50	1.39
30	0.90
45	1.22
50	1.34

Table 9 Effect of temperature on the mean droplet diameter

The temperatures are shown in the order in which the emulsion was heated, cooled and then re-heated.

This experimental sequence confirms the reversible nature of the droplet breakdown and coalescence of droplets in a shear field.

At 40°C and 50°C the mean droplet diameters are similar (i.e. 1.42 μm and 1.39 μm respectively) but on cooling the emulsion to 30°C there is a decrease in the mean droplet diameter to 0.90 μm . Increasing the temperature again to 45°C and then to 50°C causes an increase in the mean droplet diameter (i.e. 1.22 μm and 1.34 μm respectively). This agrees with the results obtained at low shear rates which showed that lower temperatures resulted in the formation of smaller droplets overall (section 4.6).

More detailed examination of the droplet size distributions show that the number of droplets below 1 μm in diameter is affected by the changes in temperature.

It can be seen from Figs 78-82 that at each temperature, the distribution of droplets below 1 μm in the emulsion remains fixed at the same percentage level; droplets below 1 μm in diameter are therefore treated as a single group and the percentage values on the y-axis are treated as arbitrary units. This treatment allows relevant comparisons to be made at different temperatures.

At 40°C the level of droplets below 1 μm is ca. 4.7 arbitrary units whereas at 50°C it is ca. 2.5. However, when the temperature is reduced to 30°C the level of droplets below 1 μm is increased to ca. 9.7. Further increases in temperature to 45°C and 50°C lead to a reduction in the number of particles below 1 μm to ca. 4.4 and 3.0 respectively.

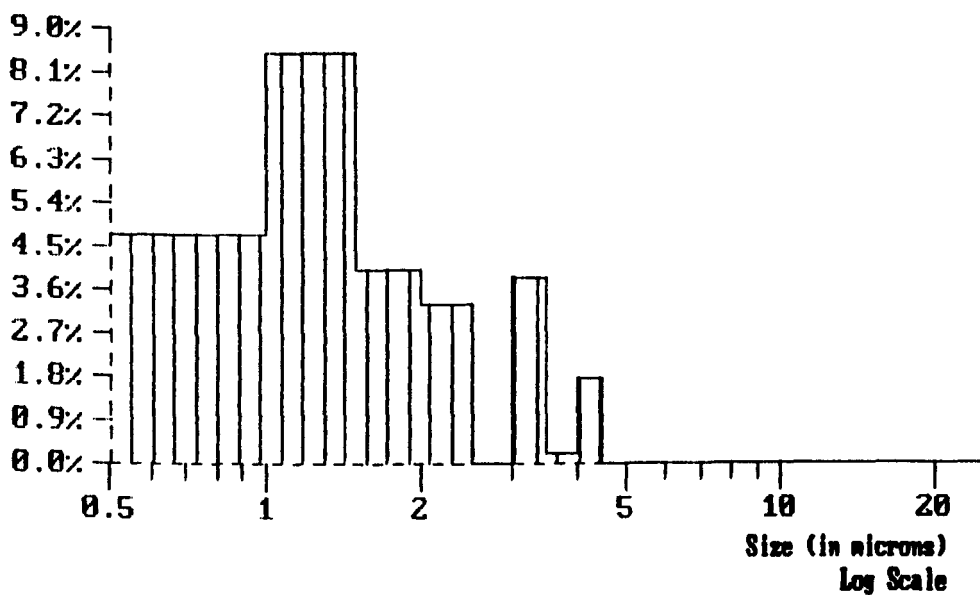


Fig 78 Droplet distribution of the hydrophilic varnish at 40°C (1st cycle)

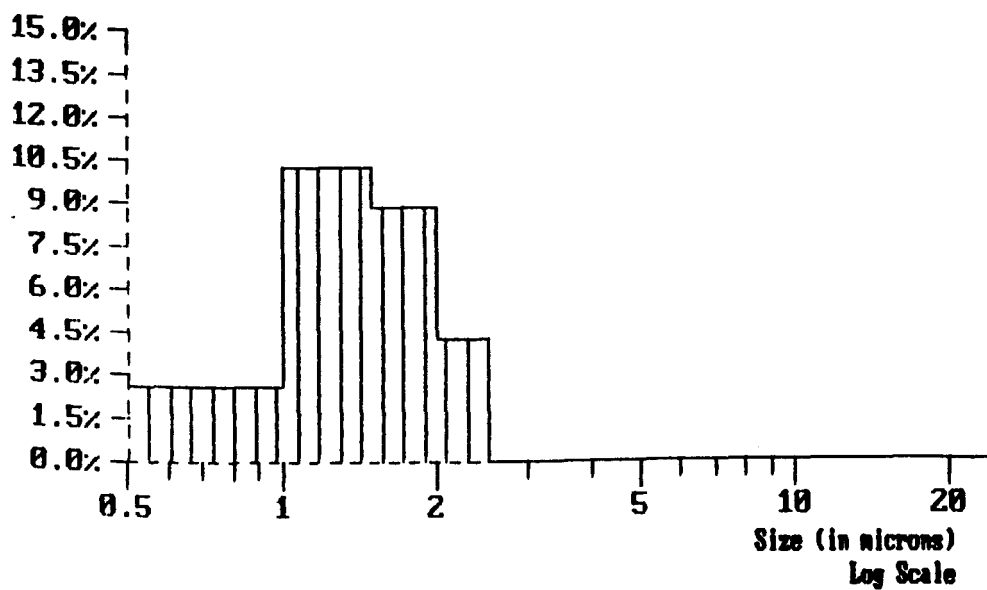


Fig 79 Droplet distribution of the hydrophilic varnish at 50°C (1st cycle)

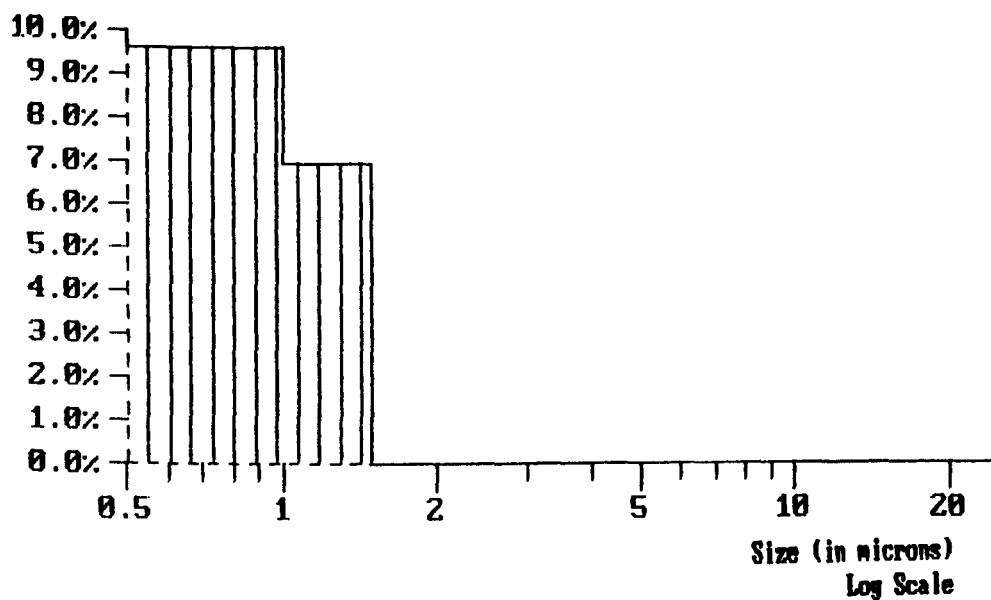


Fig 80 Droplet distribution of the hydrophilic varnish at 30°C

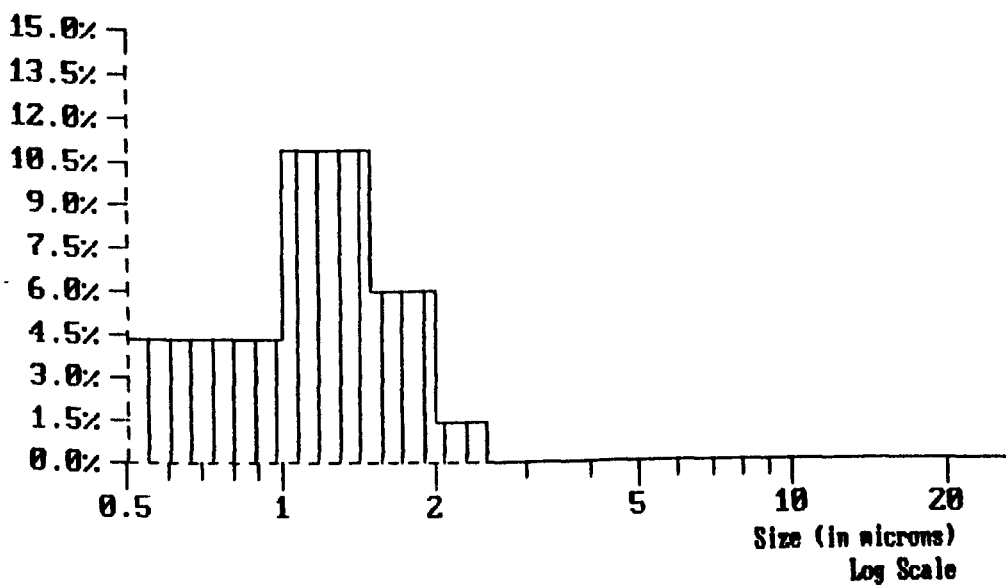


Fig 81 Droplet distribution of the hydrophilic varnish at 45°C (2nd cycle)

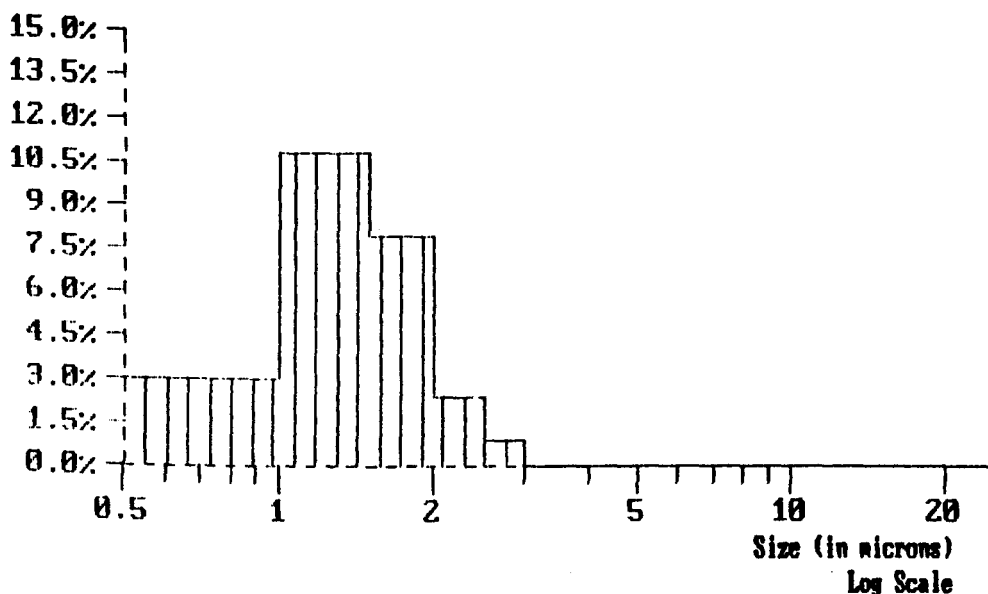


Fig 82 Droplet distribution of the hydrophilic varnish at 50°C (2nd cycle)

These results show that once the emulsion is formed, the droplet distribution is affected by changes in temperature. If such temperature changes were to occur on the press, and the droplet distribution in the emulsion was significantly altered, it could be expected that the quality of the printed image would be affected.

At higher temperatures, a greater amount of surface water would be formed as a result of the increased rate of coalescence. An excess of surface water could lead to poor ink transfer and image blinding in extreme cases. Under these circumstances, it would be necessary to reduce the water feed to the printing plate.

If however, the temperature was decreased, the production of surface water would be limited. A significant reduction in the amount of surface water could increase the risk of ink being deposited on the non-image areas of the printing plate, i.e. scumming. In order to correct the ink/water balance, the rate of water being fed to the plate would need to be increased. However, adding more water to the plate could lead to further reductions in

temperature which could increase the viscosity of the emulsion and make additional correction necessary. Under these circumstances it might be better to increase the temperature of the press by some means. This argument is less important at higher temperatures, where the viscosity is not expected to be affected greatly by further increases in temperature. Thus a correction strategy of adding water might destabilise the process. Good water balance would be particularly important at start up.

5.4 Investigation of the effects of memory on the particle size distribution

Pangalos et al¹⁹ conducted a series of experiments which showed that after shear was applied to a lithographic ink certain time-dependent memory effects were apparent. In particular, the transient response of the ink between successive applications of shear was found to be dependent upon the 'rest period' allowed between the applications of shear.

A series of experiments, using a model varnish system, was designed to examine the effects of 'rest periods' upon the breakdown of fountain solution droplets.

These experiments were carried out using three derivatives of the hydrophilic varnish, where the petroleum distillate used to dilute the varnish was altered. The following combinations were used:

- (i) Hydrophilic varnish diluted with 20% of a 1:1 mixture PKWF 6/9 and PKWF 6/9 AFN
- (ii) Hydrophilic varnish diluted with 20% PKWF 6/9
- (iii) Hydrophilic varnish diluted with 20% PKWF 6/9 AFN

PKWF 6/9 contains 15% aromatic fractions whereas PKWF 6/9 AFN is the 'aromatic free' version of this distillate.

Procedure

Hydrophilic varnish (30 g [diluted with 20% PKWF 6/9 and PKWF 6/9 AFN 1:1]) was weighed into the double-walled stainless steel beaker which was then set up as previously described (section 5). Water was circulated around the beaker at 23°C and the varnish was left to equilibrate for 30 minutes.

The varnish was stirred for 5 minutes during which time the recorded temperature reached a constant value of 34°C. Demineralised water (6 g) was then dribbled into the vortex of the varnish from a fixed-volume pipette over a period of 20 seconds. This resulted in a decrease in temperature to 29°C.

The varnish and water were stirred together for 1 minute and then allowed to rest for 1 minute. A sample of the resulting emulsion was removed at the end of the 'rest period' for testing on the Galai CIS-1. This was repeated for a total of five periods of stirring for 1 minute, each separated by 'rest periods' of 1 minute. The temperature did not fall below 26°C or rise above 29°C.

This procedure was repeated with 'rest periods' of three minutes and five minutes. The mean diameters of the water droplets were compared.

The experiment was repeated for the hydrophilic varnish diluted with 20% PKWF 6/9 and for the varnish diluted with 20% PKWF 6/9 AFN. However, although the same stirring/resting pattern was adopted as before (i.e. one minute of stirring followed by a specified 'rest period'), droplet distribution was only measured at the end of the third and fifth 'rest period'. Further results were obtained using a 'rest period' of eight minutes.

Results

As expected, the mean of the droplet diameter decreases with increasing stirring time (Table 10). After the fourth minute of stirring there is very little change in the mean droplet diameter, indicating that the emulsion is approaching a dynamic equilibrium.

Rest Period (min)	Mean Droplet Diameter (μm)				
	Stirring Time (min)				
	1	2	3	4	5
1	^a 7.35 ^b 7.32	3.88 4.12	3.4 3.71	1.71 1.88	1.48 1.84
3	^a 6.6 ^b 7.03	3.88 3.54	2.48 2.88	1.81 1.94	1.63 1.52
5	^a 10.95 ^b 11.39	5.02 4.62	2.68 2.66	2.11 2.29	2.29 2.37

Table 10 Effects of 'rest periods' on the breakdown of droplets in an emulsion prepared with a varnish containing a 1:1 mixture of PKWF 6/9 and PKWF 6/9 AFN

where:

'a' represents the first set of results recorded from the emulsion

'b' represents a second set of results recorded from the same emulsion

Comparing the results after five minutes of stirring, it can be seen that 'rest periods' of 1 minute and 3 minutes produced emulsions with similar mean droplet diameters. However, after a 5 minute 'rest period', the mean droplet diameter recorded during the first two minutes of stirring, was larger than those obtained for the shorter 'rest periods'.

This implies that within this particular varnish system, either some memory effects are apparent that influence the way in which the water droplets are broken down in the emulsion, or coalescence is taking place.

Pangalos *et al* found that increasing the duration of the 'rest period', between periods of shearing, resulted in an increase in the thixotropic response of lithographic news inks¹⁹. As this work was carried out on inks and not emulsions, it may be inferred from the present study that changes in the thixotropic response would affect the breakdown of

droplets. If the ink or varnish regains its structure, thereby increasing in viscosity, it would be expected that the rate of droplet breakdown would be increased. The time-dependency of the internal structure of the same hydrophilic model varnish that was used in this work has been studied. It was found that memory effects of a similar order (i.e. approximately 5 minutes) were present⁶⁷.

Given that droplet breakdown is greater after 'rest periods' of 1 and 3 minutes compared with that of 5 minutes, it may be concluded that time-dependent effects similar to those observed by Pangalos et al (i.e. increased thixotropic decay) are occurring within the varnish system. However, the fact that the mean droplet diameter is larger after a 5-minute 'rest period' could indicate that the structure basis for thixotropic memory effects needs to be considered in the emulsification process.

An increase in the mean droplet size indicates that coalescence is taking place. Therefore this raises the question of whether the longer 'rest period' of 5 minutes allows time for coalescence to take place within this system. If this is so, attention must be focused on the time necessary for the drainage of a film of continuous phase between two droplets; the results indicate that this must be at least 5 minutes in this particular varnish system.

It is well known that the emulsification process involves droplet breakdown and coalescence which takes place at different rates^{68,69}. In this case, the results indicate that droplet breakdown predominates up to a 'rest period' of 3 minutes, whereas coalescence dominates at longer 'rest periods'.

The results of the experiment using PKWF 6/9 are shown in Table 11.

Rest Period (min)	Mean Droplet Diameter (μm)	
	Stirring Time (min)	
	3	5
1	^a 3.25 ^b 3.23	1.83 1.74
3	^a 4.96 ^b 3.37	1.88 2.05
5	^a 2.77 ^b 2.86	1.50 1.60
8	^a 3.66 ^b 2.50	2.46 2.42

Table 11 Effects of 'rest periods' on the breakdown of droplets in an emulsion prepared with a varnish containing PKWF 6/9

where:

'a' represents the first set of results recorded from the emulsion

'b' represents a second set of results recorded from the same emulsion

Comparing the results after five minutes of stirring, it can be seen that the mean droplet diameter was similar after the 'rest periods' of one minute and three minutes. However, after a five minute rest period the emulsions formed gave a lower mean droplet diameter i.e. 1.50-1.60 microns. On increasing the 'rest period' to eight minutes it was found that the mean droplet diameter increased to 2.46-2.42 microns. These results indicate that the memory effects are most apparent at an optimum 'rest period' i.e. around five minutes where the breakdown of the water droplets appears to be enhanced.

These results can now be evaluated in the context of the work of Pangalos et al¹⁹; it may be concluded that the thixotropic response, and hence the droplet breakdown, is the predominant process up to a 'rest period' of 5 minutes for this system. However, after a 'rest period' of 8 minutes, coalescence appears to be the more dominant process.

The results of the experiments using PKWF AFN 6/9 are shown in Table 12.

Rest Period (min)	Mean Droplet Diameter (μm)	
	Stirring Time (min) 3	5
1	a3.39 b3.59	2.46 1.71
3	a2.44 b2.42	1.71 1.84
5	a3.38 b3.46	1.83 2.04
8	a3.61 b2.50	1.29 1.10

Table 12 Effects of 'rest periods' on the breakdown of droplets in an emulsion prepared with a varnish containing PKWF 6/9 AFN

where:

'a' represents the first set of results recorded from the emulsion

'b' represents a second set of results recorded from the same emulsion

Comparing the results after 5 minutes of stirring it can be seen that, generally, the mean droplet diameter is reduced as the length of the 'rest period' is increased. It would appear that the memory effects last longer in this system than in the previous two systems.

It is possible that in this system the thixotropic response (and hence the extent of droplet breakdown) increases with lengthening 'rest periods'. Further work would be required to establish whether the coalescence would begin to dominate the process at longer 'rest periods'.

Each of the modified varnishes were found to have similar viscosities, e.g. ca. 15 Pas at 23°C with a shear rate of 200 s⁻¹. In view of the results showing how viscosity affects the amount of heat generated by the stirring conditions (section 5.1), it may be assumed that any temperature variations within the varnish system were similar.

5.5 Conclusions

Coalescence appeared to be the dominant process in the varnish diluted with PKWF 6/9 when allowed a longer 'rest period'; this was accounted for by the persistence of the film between two water droplets that are in contact with each other. The aromatic content of PKWF 6/9 may be expected to have greater surface activity which could account for the longevity (i.e. up to 8 minutes) of the film of varnish between the droplets.

The varnish diluted with the aromatic-free distillate (i.e. PKWF 6/9 AFN) gives no indication of coalescence over the 'rest periods' examined. Instead, this varnish appears to be capable of regaining more of its structure with increasing 'rest periods'. It is possible that the increased structure, which may be accompanied by an increase in viscosity, is sufficient to overcome any coalescence that might have occurred by breaking down these and any other droplets after stirring was started again.

At any given time after the start of the experiment, there is a distribution of the water droplet/varnish configurations. In these configurations the varnish provides a cavity/shell around the water droplet which is linked by the interface. This interface will be in various stages of distortion, from a stable sphere through to a spheroid to various

'dumbbell' shapes and on to fragmentation. Thus, at any given time, there will be a proportion which has not distorted and a proportion at various stages of distortion.

The longer the shearing process is sustained the greater will be the fragmentation (until a coalescence process becomes sufficient to cause a dynamic equilibrium to be attained). If, however, the shearing process is interrupted, the distorted interface structures can relax. If this interruption is long enough, i.e. corresponding to the lifetime of the appropriate memory effects, then fairly complete relaxation will take place and there would be no contribution to fragmentation from the distorted interface component.

Considering the continuous phase only, it is known that the ink and the varnish base are thixotropic, thus the viscosity is restored during a 'rest period' when the shear stress is removed.

Consider, therefore, an ink or varnish in which some large water particles are distributed. The above argument suggests that the use of 'rest periods' would ensure higher viscosity ratios during the shearing regimes, thus resulting in smaller particles. The experimental evidence however, is different with the 'rest periods' allowing increased opportunities for coalescence.

The question now arises of whether these results are relevant to the processes occurring on the printing press. Consider the situation where a press has been restarted after a stoppage. Briefly, this will mean that the free surface water content will be expected to increase during the stoppage. This water may then evaporate and the overall effect is a reduction in the water available for dampening the non-image areas when the press restarts thus, giving rise to scumming.

6 The effects of IPA on emulsification

The use of IPA in lithography is widespread but its mechanisms have yet to be clarified. It is therefore useful to examine the effects of IPA within the context of this study i.e. in terms of emulsion formation and droplet distribution.

This series of experiments has been conducted under low shear conditions with the Moulinex stirrer and under high shear conditions with the Dispermat.

Generally, IPA is added at concentrations of up to 20% of the fountain solution on a conventional press⁴³; however, this is believed to allow for a certain amount of alcohol that is lost through evaporation. There are several instances of IPA being used at concentrations ranging from 8% to 15% under experimental conditions^{34,43}. It was decided that for the purposes of this study, a 10% IPA solution (by weight) should be used as a fountain solution, with demineralised water acting as the control fountain solution.

6.1 Determination of droplet distributions within varnish emulsions containing IPA under low shear rate conditions

Materials

Hydrophilic varnish

Demineralised water

10% IPA solution

Procedure

IPA (10 g) was mixed together with demineralised water (90 g) in a 250 cm³ powder jar.

The solution was left to cool to room temperature.

Hydrophilic varnish (30 g) was weighed into a 50 cm³ powder jar, covered with 'parafilm', placed in a water bath set at 40°C and left to acclimatise for approximately 45 minutes. A 10% IPA solution (3 g) was added to the varnish and the mixture stirred for 1 minute at 900 rpm.

A sample of the resulting emulsion was removed and tested on the Galai CIS-1 according to the procedure described in section 3.8.2.

The same mixture was re-stirred and tested as above for cumulative stirring times of 2, 3, 4 and 5 minutes.

A control experiment was also carried out under identical conditions where hydrophilic varnish (30 g) was mixed with demineralised water (3 g). Samples were removed after 1, 2, 3, 4 and 5 minutes of stirring and tested on the Galai CIS-1.

The mean droplet diameter was plotted against stirring time for both fountain solutions (Fig 83).

Results

The plots of mean droplet diameter against time for the IPA and the demineralised water containing varnish emulsions show that the breakdown of fountain solution droplets is similar, in so far as mean drop diameters are concerned.

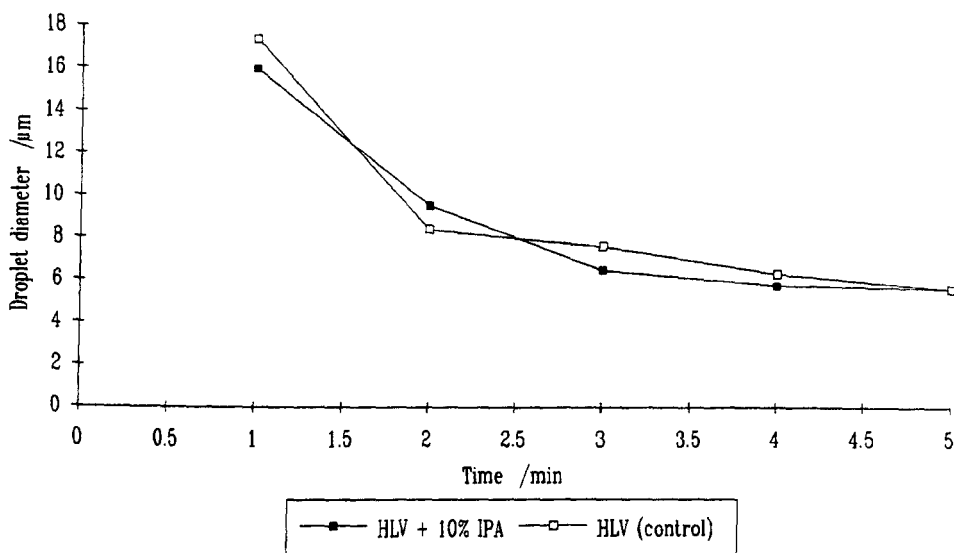
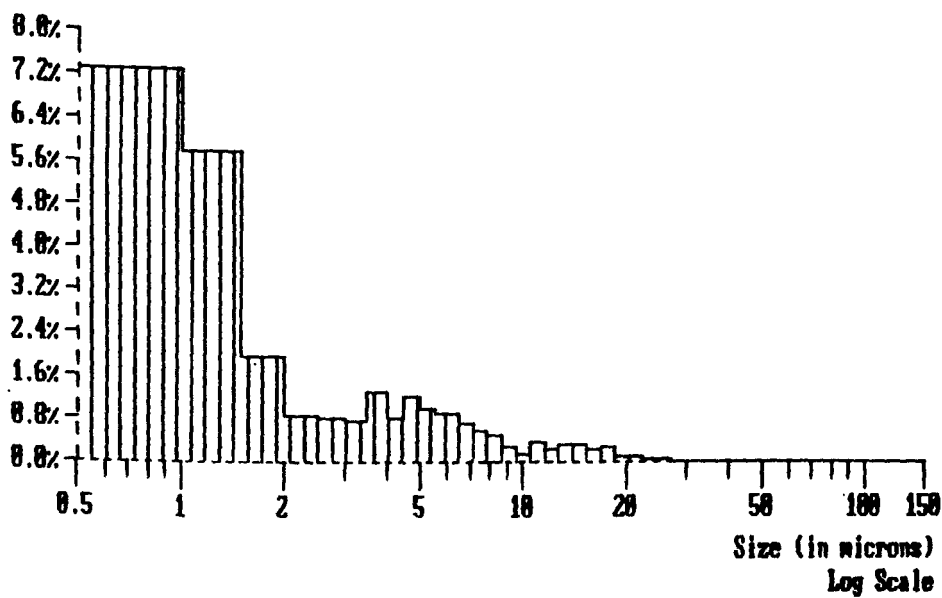


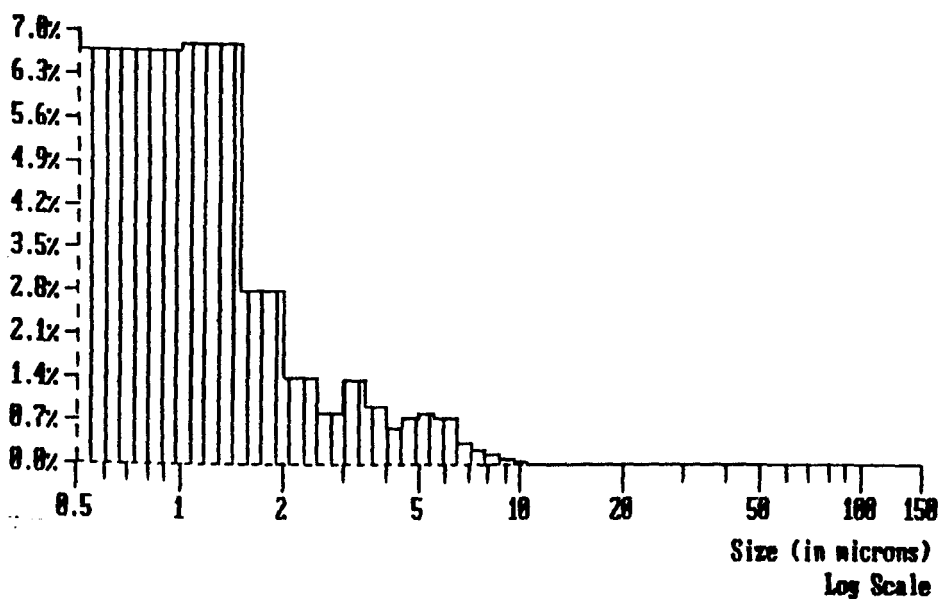
Fig 83 Comparison of the emulsification of varnish containing a 10% IPA solution with a varnish containing demineralised water

However, a comparison of the graphs showing the droplet size distribution, i.e. the number distribution (Figs 84-93), shows that there are some differences between the two samples.

Between the cumulative stirring times of 1 and 3 minutes (Figs 84-89), it can be seen that the 10% IPA fountain solution produced emulsions which contained a greater proportion of droplets below 2 μm in diameter compared with the corresponding control samples.

However, after 4 and 5 minutes of stirring the situation is reversed, with the number of droplets below 2 μm being greater in the control samples than in the emulsions containing IPA (Figs 90-93). The presence of IPA has resulted in a smaller proportion of droplets below 2 μm in diameter, and a larger proportion of droplets above 2 μm in diameter compared with emulsions formed with demineralised water.





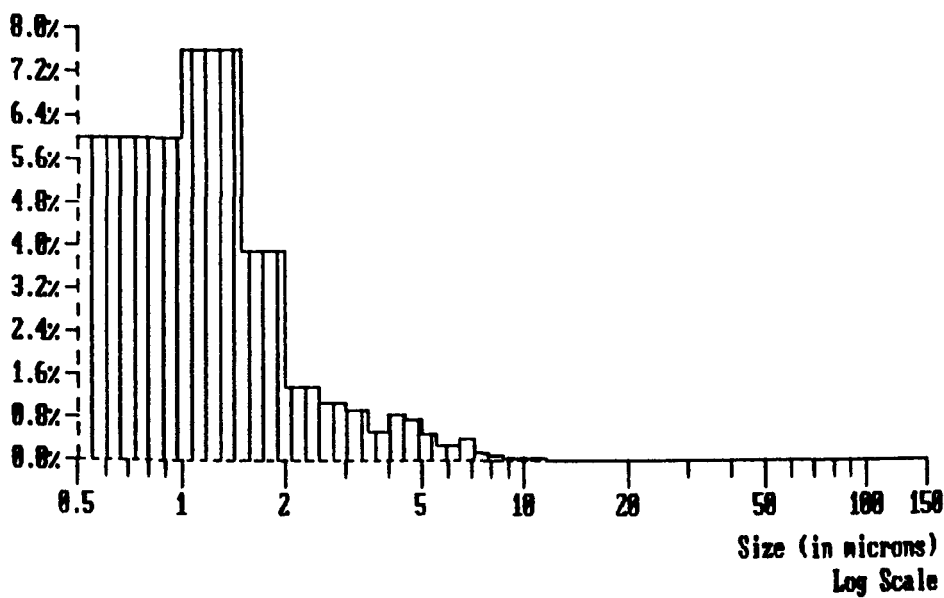


Fig 88 Number distribution of water/varnish emulsion after stirring for 3 minutes

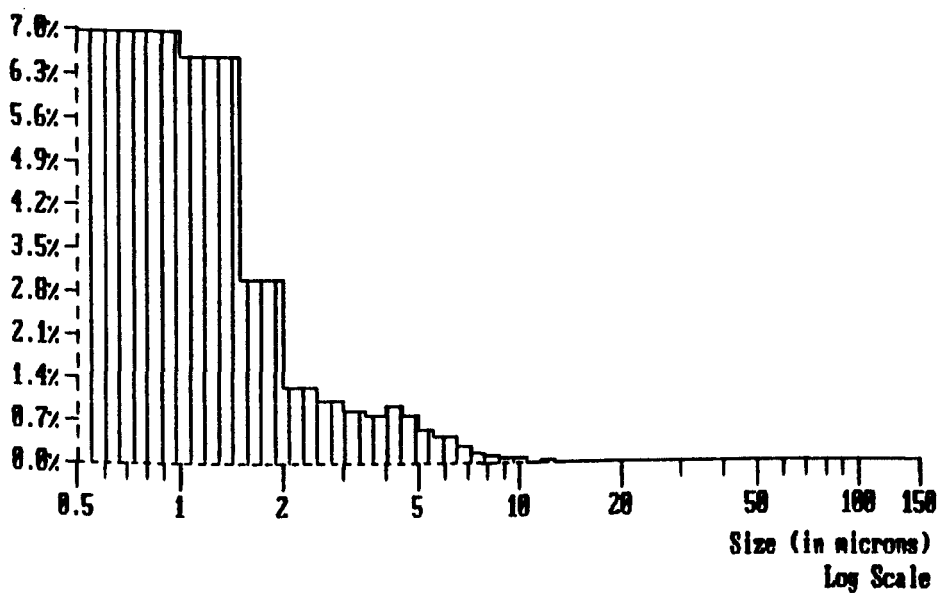


Fig 89 Number distribution of emulsion containing IPA after stirring for 3 minutes

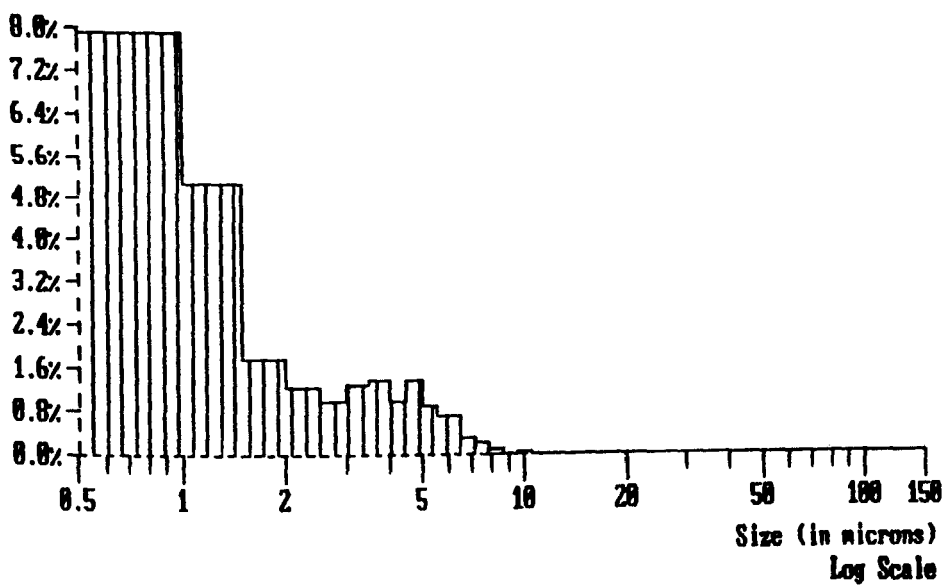


Fig 90 Number distribution of water/varnish emulsion after stirring for 4 minutes

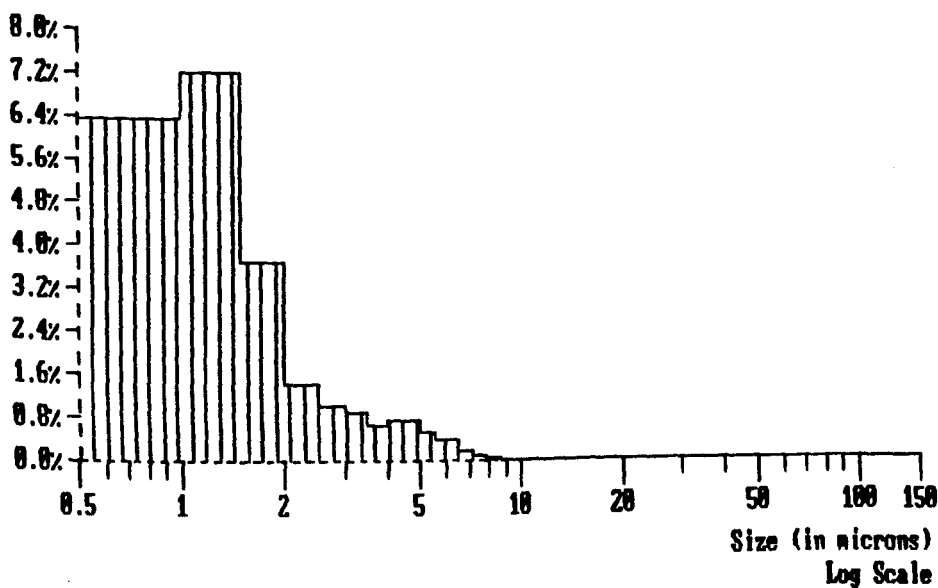


Fig 91 Number distribution of emulsion containing IPA after stirring for 4 minutes

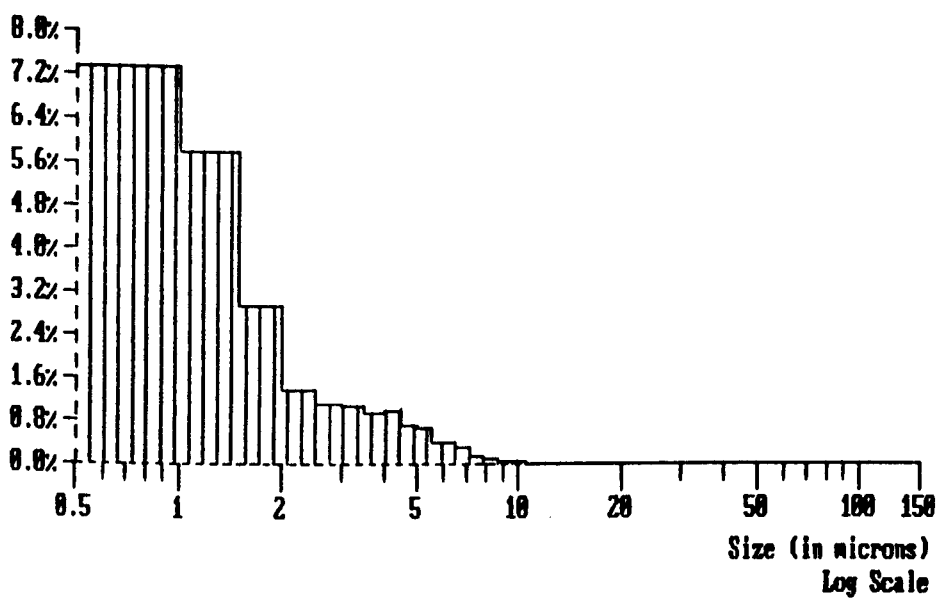


Fig 92 Number distribution of water/varnish emulsion after stirring for 5 minutes

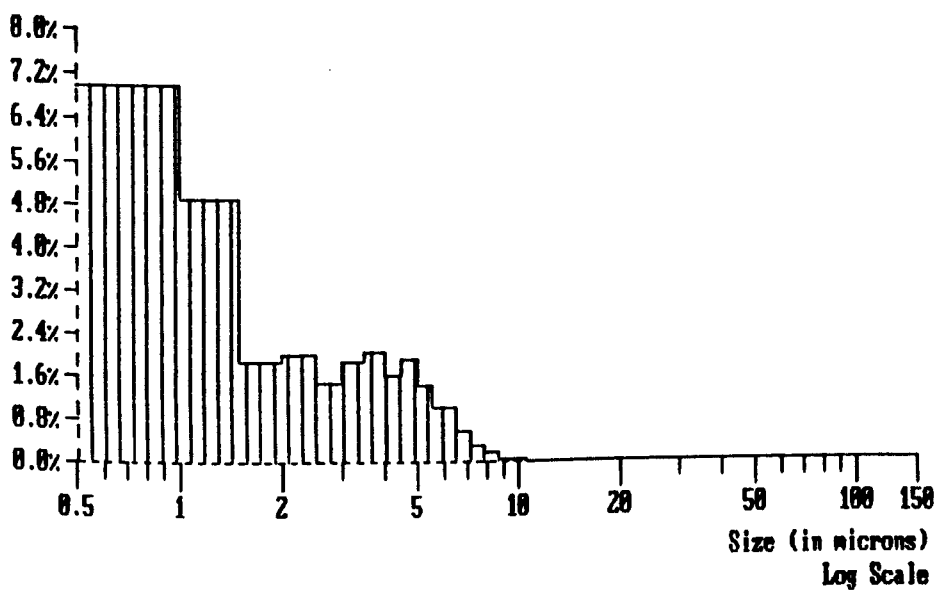


Fig 93 Number distribution of emulsion containing IPA after stirring for 5 minutes

In addition, a comparison of the distribution of fountain solution droplets after 5 minutes of stirring is particularly interesting given that the mean droplet diameters are similar i.e. 5.65 μm with IPA and 5.63 μm in the absence of IPA (Figs 94 and 95 respectively).

It can be seen that the distribution of the demineralised water droplets is skewed towards the smaller droplets; by comparison, the distribution of the droplets containing IPA appears to be more indicative of a 'normal' Gaussian distribution.

This observation is in agreement with those made by Braun³⁴ and Iwaki⁴². In studies comparing the emulsification of printing inks with water and IPA solutions, they found that the presence of IPA led to the formation of emulsions that were of 'uniform' appearance i.e. a broad distribution was found.

However, in addition to this they also reported that the droplets formed were finer in appearance. This agrees with the findings for the IPA solution/varnish emulsion obtained after 1, 2 and 3 minutes stirring but not with the results obtained after 4 and 5 minutes of stirring.

The action of IPA in this case appears to be time-dependent, with the increase in the broader distribution of the emulsion being seen only after the first 4 minutes of stirring. It would therefore appear that IPA inhibits the droplet breakdown and suppresses the formation of smaller droplets, thus giving rise to a more uniform emulsion.

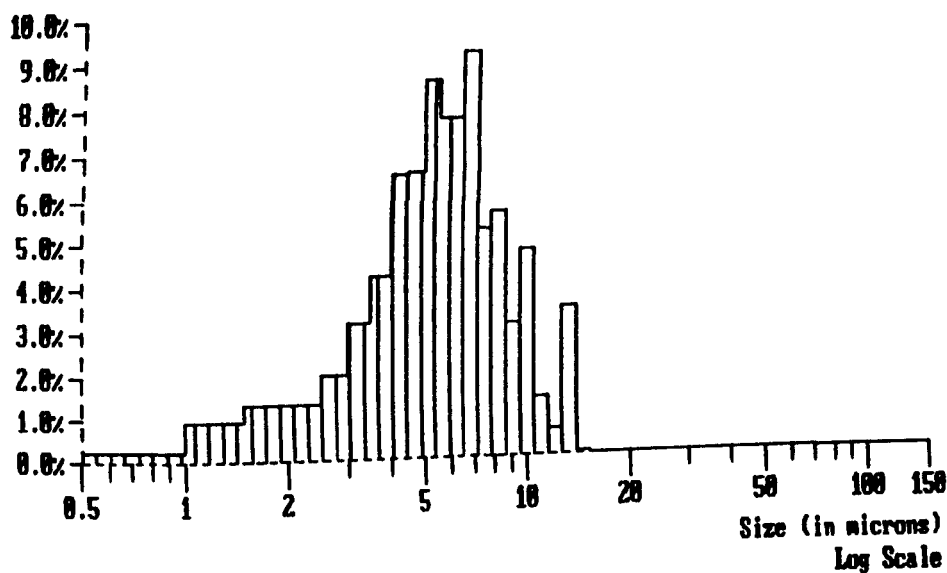


Fig 94 Droplet distribution of water/varnish emulsion after stirring for 5 minutes

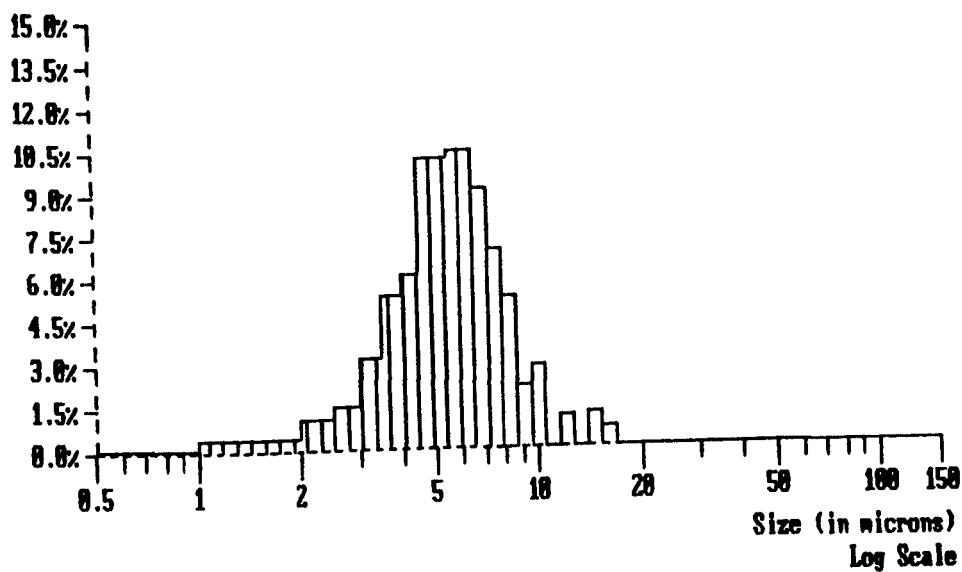


Fig 95 Droplet distribution of emulsion containing IPA after stirring for 5 minutes

6.2 Determination of the effect of IPA concentration on the interfacial tension between the varnish and fountain solution

Having examined some effects of IPA on the emulsification of the model varnish, it would be useful to investigate how the concentration of IPA affects the interfacial tension between the fountain solution and varnish. This experiment was carried out on the hydrophilic and hydrophobic varnish.

Materials

Hydrophilic varnish

Hydrophobic varnish

Demineralised water

IPA solutions

Procedure

Solutions of IPA in demineralised water were prepared at the following concentrations: 1, 5, 7, 10 and 15% (by weight).

The interfacial tension between the diluted varnish (section 3.9.2) and each IPA solution was measured at 40°C and a flow rate of 4.56 mm³s⁻¹. Demineralised water was used as a control and represented a 0% IPA solution. Measurements were repeated three times at each concentration of IPA. The average of the three measurements is reported.

A graph of interfacial tension against IPA concentration was plotted (Fig 96).

Results

It can be seen that there is a decrease in interfacial tension with increasing IPA concentration for both varnishes; this is to be expected.

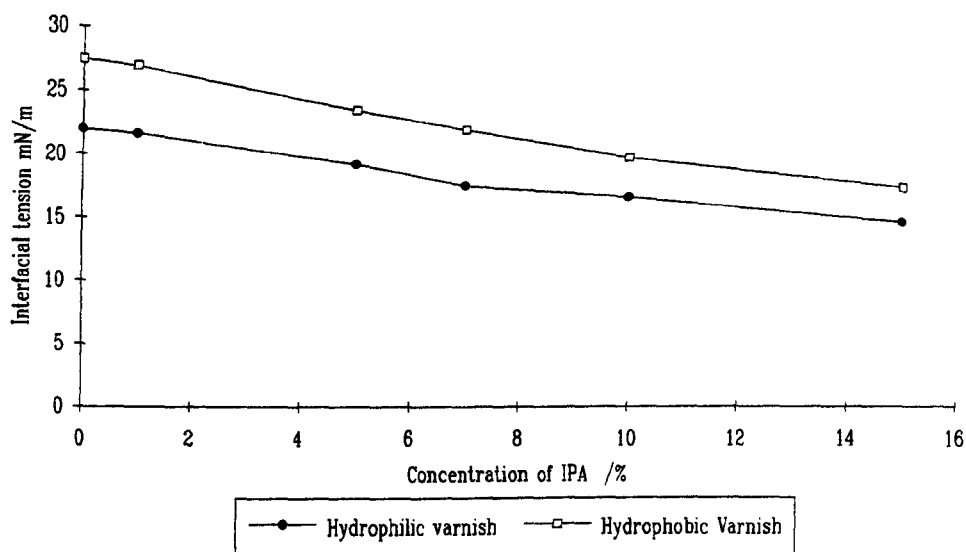


Fig 96 Interfacial tension v IPA concentration

In order to correlate this work with the results of the low shear rate emulsification studies it is necessary to consider the situation at 40°C. The interfacial tension between the 10% IPA solution and the hydrophilic varnish was found to be 16.65 mNm⁻¹, whereas the interfacial tension between demineralised water and the hydrophilic varnish was found to be 21.98 mNm⁻¹.

Consider the effect of temperature on the interfacial tension of the demineralised water/hydrophilic varnish system (section 4.7). The interfacial tension between the hydrophilic varnish and demineralised water was found to be 26.6 -16.2 mNm⁻¹ over the range of 21-70°C. The interfacial tension at the 10% IPA solution/varnish interface at 40°C (i.e. 16.6 mNm⁻¹) is comparable with the demineralised water/varnish interface at 70°C (16.2 mNm⁻¹). Thus, the effects of 10% IPA and a temperature rise to 70°C, have a similar effect on the interfacial tension between the fountain solution and the varnish.

6.3 Effects of IPA on emulsification under high shear rate conditions

Under low shear rate stirring conditions, it was found that the addition of a 10% IPA solution to the varnish affected the distribution of the fountain solution droplets throughout the emulsion. There were also indications that this effect was time-dependent. However, this time-dependency may occur simply as a result of the stirring speed applied during the test.

Under press conditions, high shear rates are applied. It is therefore most important to determine whether similar effects will be seen if these experiments are conducted under high shear rate dispersion conditions.

6.3.1 Determination of the effects of IPA on emulsification under high shear rate conditions

Materials

Hydrophilic varnish diluted with 20% PKWF 6/9

Hydrophilic varnish diluted with 20% PKWF 6/9 AFN

10% IPA solution in demineralised water

Demineralised water

Procedure

The diluted varnish (30 g) was weighed into the double-walled stainless steel beaker. A thermocouple was attached to the stationary outer shaft of the Dispermat so that the end was immersed below the surface of the varnish and towards the wall of the beaker. Water was circulated around the beaker at 23°C. The varnish was left to equilibrate for 30 minutes.

The varnish was stirred for 5 minutes until a steady temperature was reached i.e. 31°C.

The fountain solution (6 g) was dribbled from a fixed-volume pipette into the vortex of the varnish over a period of 20 seconds, during which the temperature of the mixture dropped to 29°C. Stirring was continued for 1 minute.

The emulsion was allowed to rest for 1 minute and then stirred for a further minute. This stirring cycle was continued until a total of five 1-minute periods of stirring had elapsed. Samples were removed at the end of the third and fifth 'rest periods' for testing on the Galai CIS-1. During the stirring period, the temperature did not fall below 26°C or rise above 29°C.

This procedure was adopted for all four IPA solution/varnish and demineralised water/varnish combinations.

Results

As expected, the droplet size decreased with increasing stirring time irrespective of the type of varnish or fountain solution used. This is illustrated by comparing the droplet size distribution at 3 and 5 minutes for both diluted varnishes in the presence of IPA (Figs 97 and 98).

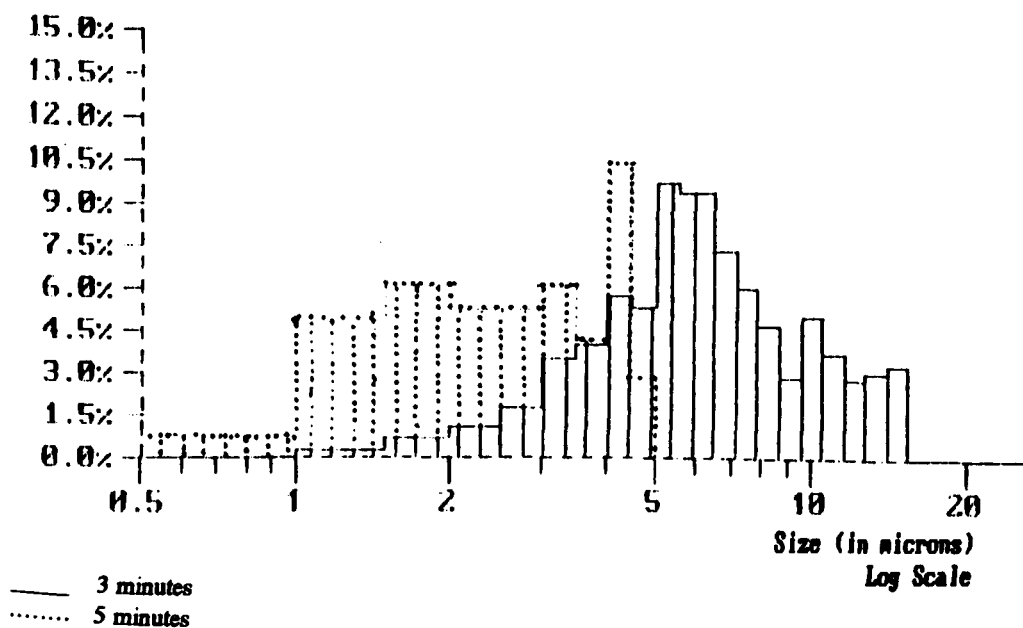


Fig 97 Droplet distribution after 3 and 5 minutes stirring for the PKWF 6/9 varnish with IPA

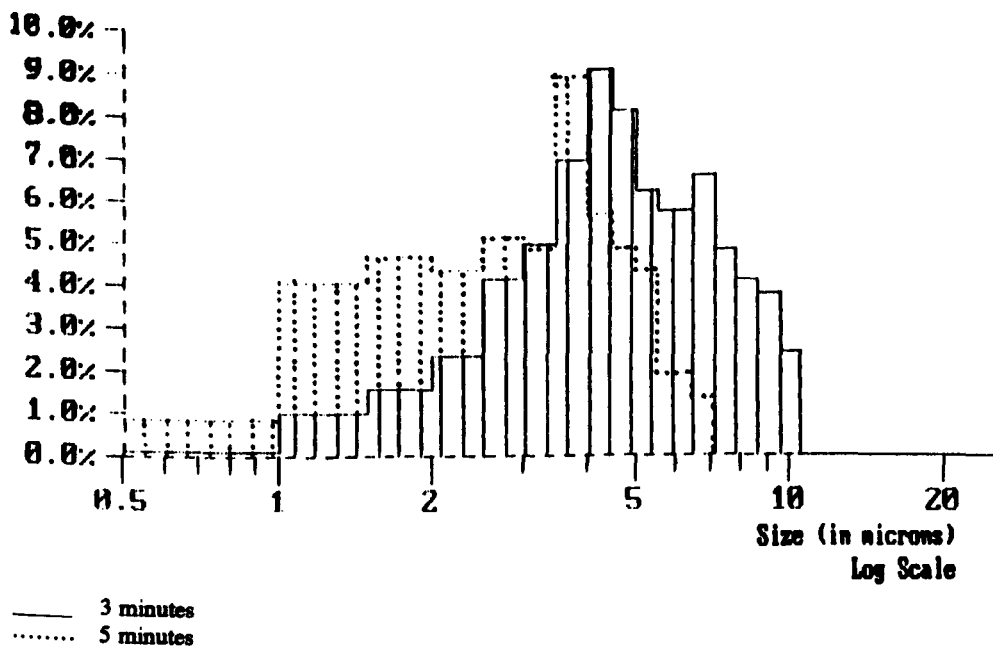


Fig 98 Droplet distribution after 3 and 5 minutes stirring for the PKWF 6/9 AFN varnish with IPA

The effect of IPA on the droplet size distribution of the varnish containing PKWF 6/9 after 3 and 5 minutes is shown in Figs 99 and 100 respectively.

After 3 minutes of stirring, the maximum droplet diameter for the emulsion without IPA was approximately 9 μm . However, in the presence of IPA the maximum droplet diameter was approximately 16 μm . Droplets below 5 μm were present in greater abundance in the emulsions without IPA.

After 5 minutes of stirring, the maximum droplet diameter (with and without IPA) was similar i.e. approximately 6 μm . However, droplets below 2 μm in diameter were present in greater abundance in the emulsions without IPA.

In the PKWF 6/9 AFN varnish system similar trends were found. After 3 minutes of stirring, the maximum droplet diameter for the emulsion without IPA was ca. 6.5 μm ; this compares with a value of ca. 10 μm for the emulsion containing IPA (Fig 101). Droplets below 2 μm in diameter were present in greater abundance in the emulsion without IPA.

After 5 minutes stirring, the maximum droplet diameter (with and without IPA) was similar, i.e. approximately 7 μm (Fig 102). However, droplets below 2 μm in diameter were present in greater abundance in the emulsion without IPA.

These results indicate that for up to 3 minutes of stirring, the breakdown of droplets appears to be inhibited by the presence of IPA. Overall, the observations made in the high shear rate studies are similar to those made in the low shear rate studies; i.e. both studies have shown that after 5 minutes of stirring there are fewer droplets below 2 μm in diameter where IPA has been used. This implies that the mechanisms of droplet breakdown in the varnish systems are not wholly dependent on the speed of stirring. Given that the viscosity of the varnish is significant to the breakdown of the water droplets, the effects of IPA on the viscosity needs to be considered.

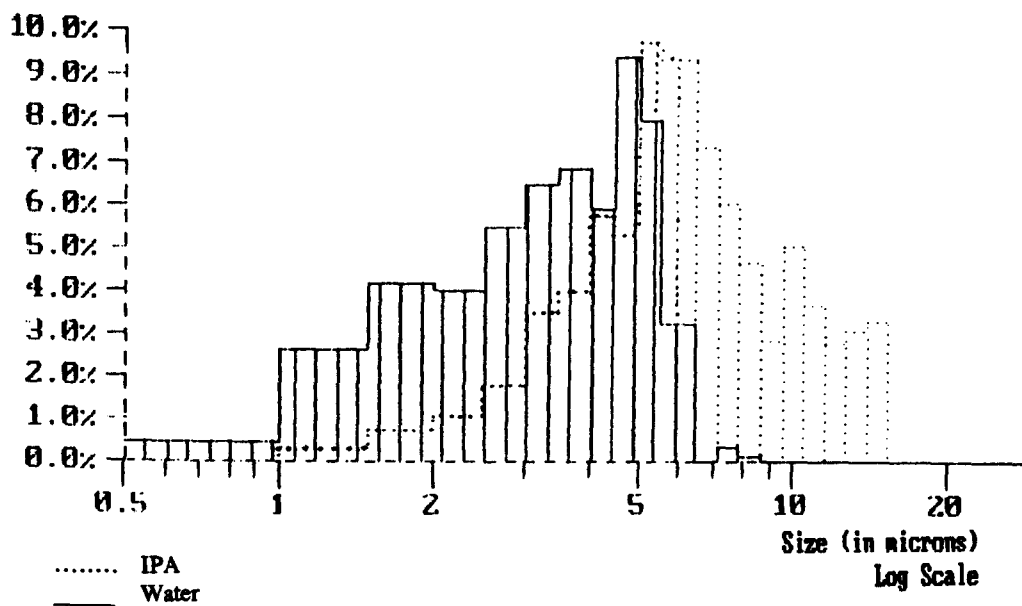


Fig 99 Comparison of the droplet distribution after 3 minutes stirring for the PKWF 6/9 varnish with and without IPA

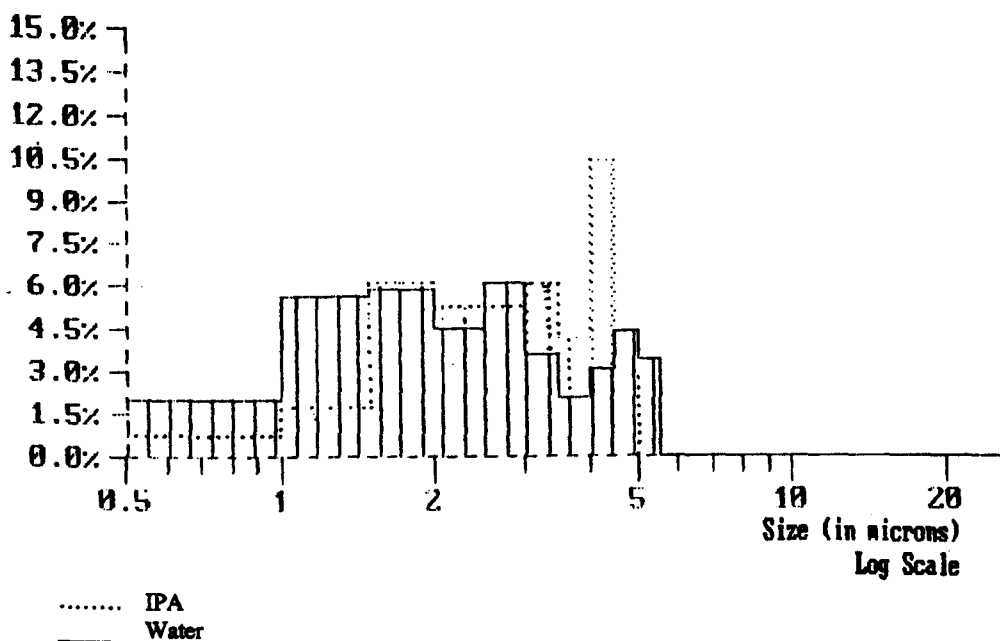


Fig 100 Comparison of the droplet distribution after 5 minutes stirring for the PKWF 6/9 varnish with and without IPA

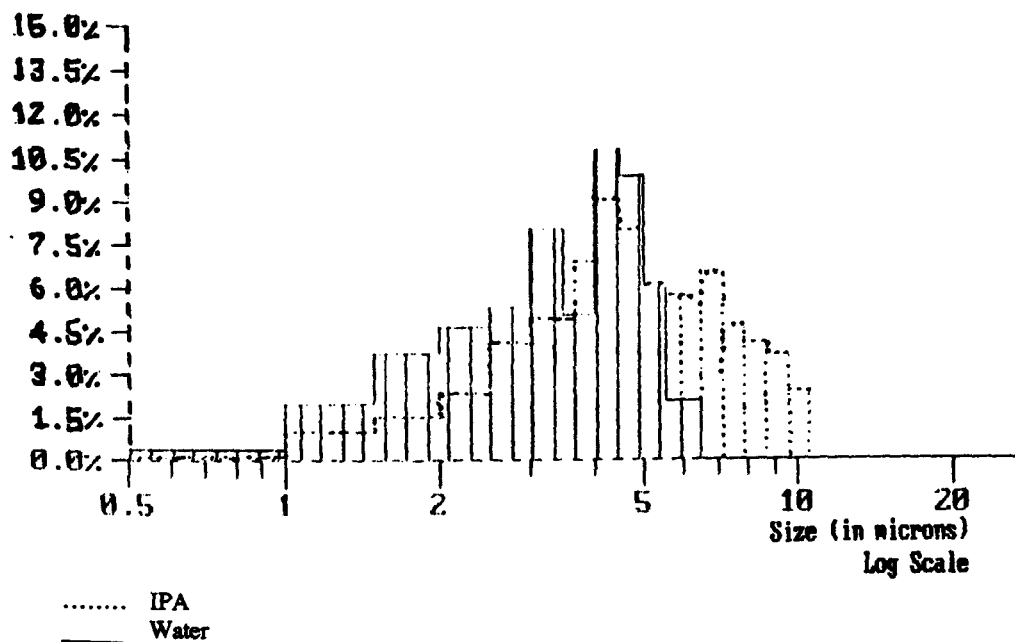


Fig 101 Comparison of the droplet distribution after 3 minutes stirring for the PKWF 6/9 AFN varnish with and without IPA

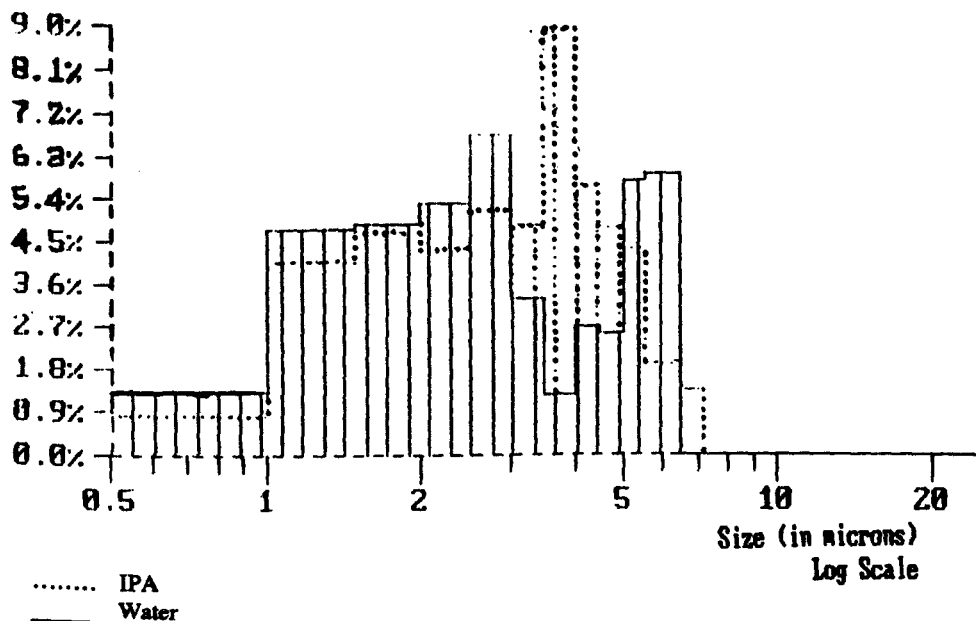


Fig 102 Comparison of the droplet distribution after 5 minutes stirring for the PKWF 6/9 AFN varnish with and without IPA

6.4 Effects of IPA on the viscosity of the varnishes

A reduction in interfacial tension should promote the formation of an emulsion. Clearly, the reduction in the interfacial tension of the fountain solution/model varnish systems due to the addition of a 10% IPA solution is not sufficient to cause this effect (section 6.2).

The reduction in the surface tension of a fountain solution resulting from the addition of IPA has been found to improve the wetting of the printing plate. Thus, the interfacial tension plays an important role in the interaction between the plate and the fountain solution in lithography. However, the role of the IPA solution in establishing the ink/water balance in the model varnish systems does not appear to be linked to its ability to reduce the interfacial tension. In view of this conclusion, other effects of IPA upon the fountain solution/model varnish emulsion need to be examined.

Douw and Blokker²⁷ found that the addition of IPA to a lithographic printing ink caused the ink to become 'softened'. They reported that the addition of 1% IPA to a fountain solution led to a 50% decrease in the viscosity of an ink.

Given the fact that these studies have shown that the viscosity of the varnishes affects the way in which the droplets of fountain solution are broken down, and that IPA affects the distribution of the fountain solution, the observations of Douw and Blokker²⁷ need to be investigated within the context of the present study.

The limited availability of the model hydrophilic and hydrophobic varnishes did not permit the effects of IPA to be measured on these materials; however, experiments were carried out with the LTHS varnish and also with a commercial varnish supplied by Usher Walker. In view of the previous results throughout section 4, it is reasonable to assume that the LTHS varnish would behave in a similar fashion to the hydrophilic varnish.

6.4.1 Determination of the effects of IPA on the viscosity of the varnishes

Materials

LTHS varnish

Usher Walker heat-set lithographic varnish

Demineralised water

10% IPA solution

Procedure

6.4.2 Preparation of the varnish emulsions

Varnish (30 g) was placed in the double-walled stainless steel beaker. Water was circulated around the beaker at 23°C. The varnish was stirred until it reached a constant temperature i.e. 5 minutes (31°C). Fountain solution (6 g) was added from a fixed-volume pipette to the vortex of the varnish over 20 seconds. The mixture was stirred for a further 5 minutes.

The emulsion was allowed to stand for 10 minutes before its viscosity was measured.

6.4.3 Determination of the viscosity of the varnish emulsions

The Carri-Med CSL 100 rheometer was set up at 23°C with a cone and plate geometry: cone diameter 2 cm; cone angle 1°.

The emulsion (ca. 2 g) was placed on the rheometer which was programmed to run at a constant stress of 1000 Pa over a 3-minute period.

The viscosity was plotted against time.

Results

For both varnish types the presence of IPA in the fountain solution has produced emulsions of lower viscosity than those obtained with demineralised water only (Figs 103 and 104). The viscosity of the emulsion formed between the LTHS varnish and the IPA solution was approximately 30% lower than the emulsion produced with demineralised water. The viscosity of the emulsion formed with the Usher Walker varnish and the IPA solution was 50% lower than the corresponding emulsion produced with demineralised water.

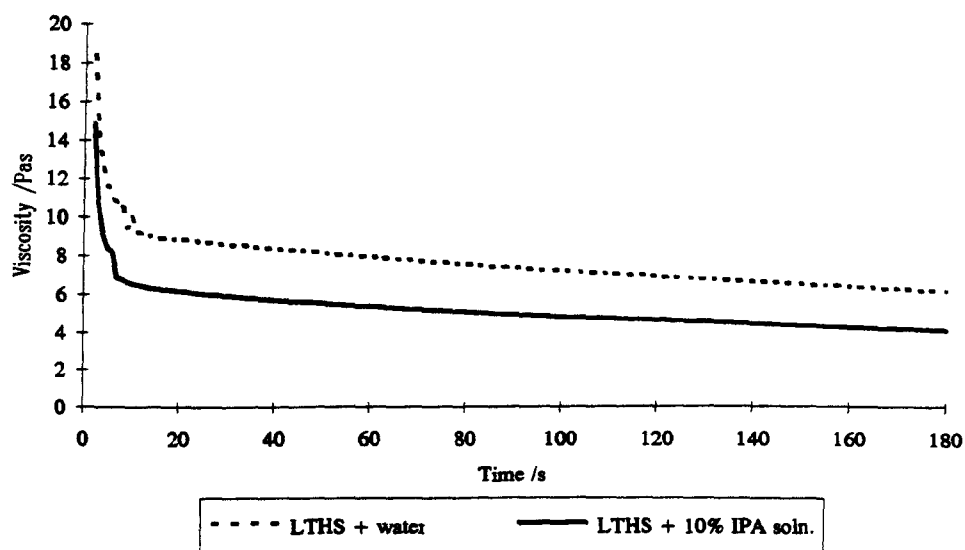


Fig 103 Comparison of the viscosities of a demineralised water/LTHS varnish emulsion with a 10% IPA solution/LTHS varnish emulsion

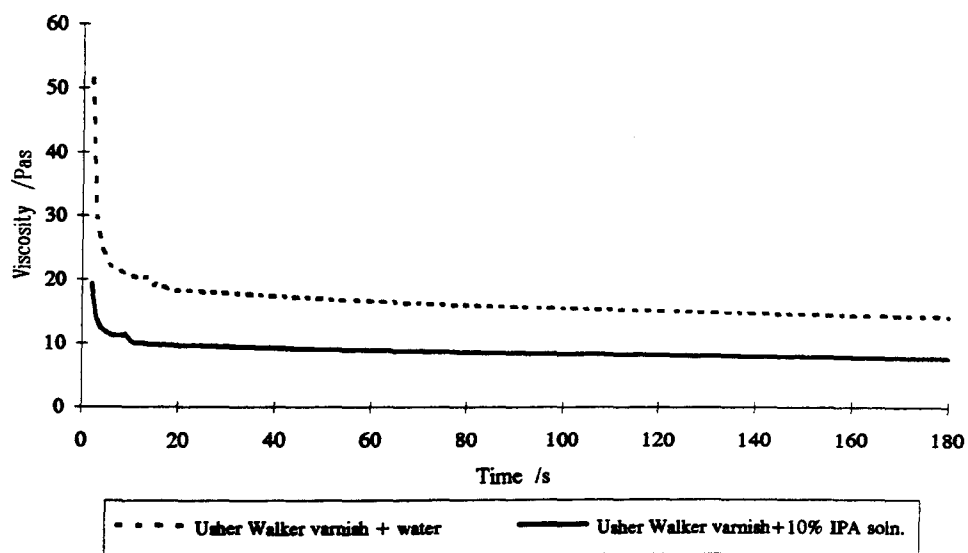


Fig 104 Comparison of the viscosities of a demineralised water/Usher Walker varnish emulsion with a 10% IPA solution/Usher Walker varnish emulsion

6.5 Discussion

Since it was found that the breakdown of water droplets is influenced by the difference between the viscosity of the fountain solution and the model varnishes, the fact that IPA reduces the viscosity and alters the droplet distribution of the resulting emulsion is of interest.

The studies of Bock⁴⁴ have shown that whereas IPA lowers the surface tension of the fountain solution, it does not affect the emulsification process in the same way as a classical surfactant. Thus, it was found that where cationic surfactants were used at low levels (e.g. 1% surfynol 61), the amount of fountain solution absorbed was increased. This led to over-emulsification of the ink which caused tinting during printing trials. An interesting aspect of this experiment was the similarity in surface tension between the 20% IPA solution and the 1% solution of surfynol, i.e. 25 and 26 mNm⁻¹ respectively. This indicates that the reduction in the surface tension of a fountain solution arising from the addition of IPA may not be a significant factor in the mechanism of the breakdown of fountain solution droplets. The effects of the volatility of IPA were also investigated. The emulsification properties of IPA were compared with those of surfactants which had differing rates of evaporation; these surfactants also caused over-emulsification of the printing ink.

Douw and Blokker²⁷ proposed that IPA caused the structure of lithographic inks to break down, thus leading to a reduction in viscosity. However, given that under press conditions the ink and the fountain solution (containing IPA) are only in contact with each other for a short time before the emulsion is printed, one might question whether it would be possible for such a breakdown to occur. In order to seek a satisfactory explanation for this reduction in viscosity, the situation at the fountain solution/varnish interface should be examined.

The reduction in the number of smaller droplets (i.e. below 2 μm in the low shear work) where IPA was used needs to be considered. It is estimated in this work that there is a shortfall of approximately 16.8% droplets in the range of 0.5-2 μm (where 0.5 μm represents the limit of resolution of the Galai CIS-1). This immediately raises the question of how this discrepancy can be accounted for. There are two main possible explanations for this observation. Firstly, it may be that the droplets were broken down below the resolution limit of the instrument, thus forming micro-emulsions. Secondly, the formation of droplets within this range has been affected by some means. Each of these possible explanations is now discussed.

A simple explanation might be that the IPA, on lowering the interfacial tension, enhances the potential for micro-emulsification. The formation of such micro-emulsified moieties would be expected to deplete the smallest emulsion particle size population. Such micro-emulsions are known to exist and have been studied by freeze-fracture electron microscopy e.g. Bassemir⁷⁰.

However, alternative possibilities are explored here. First of all, the distinction between a surfactant and co-surfactant needs to be examined in this context. According to De Gennes and Taupin⁷¹, co-surfactants dissolved in an aqueous phase can attack the interface and destabilise it. This would occur through a reduction of the 'persistence length' (a reduction of rigidity) or an increase in fluidity at the interface. This could lead to an increase in small particle sizes by the formation of micro-emulsions. This prediction can only be verified through further studies involving the use of light scattering or freeze-fracture analytical techniques^{72,73}.

Philips et al⁷⁴, studied the role of dynamic interfacial effects on droplets in a shear field. They proposed that surface active agents, either present as contaminants or as constituents in solutions, give rise to dynamic interfacial effects which can seriously alter the transmission of stress at the interface of a droplet. Such influences can arise from compositional effects (i.e. surface tension gradients) or from intrinsic rheological effects.

In an attempt to examine these effects further, Flumerfelt⁷⁵ found that the presence of surface active agents affected the behaviour of a droplet in a shear field. The predicted deformation, orientation and circulation behaviour of droplets was found to have been altered. These alterations were brought about by the changes in elastic effects and the surface viscous effects at the interface.

As the present study has shown that the rheology of the varnish dominates the breakdown and coalescence of droplets in the system, the work of Philips et al⁷⁴ and Flumerfelt⁷⁵ is now applied to the breakdown of droplets in the model varnish systems. However, this is combined with a further concept, where the fluidity of the interface is restricted to the non-polar hydrocarbon side of the interface. A theoretical concept emerges from these combined studies which can account for the observations concerning the effect of IPA on the emulsification of the system.

Consider the propan-2-ol molecule:

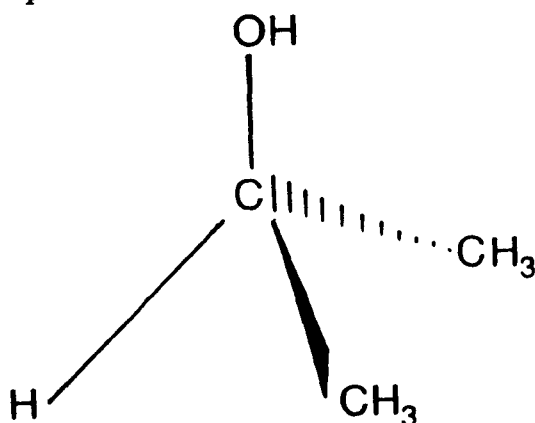


Fig 105 The propan-2-ol (IPA) molecule

The polar hydroxyl group is capable of forming hydrogen bonds with water, whereas the two methyl groups and the central methine group (i.e. the hydrocarbon groups) are capable of interacting with the hydrocarbon chains in the model varnish system.

Where propan-2-ol is added to demineralised water the molecules will become orientated at the water/vapour interface as shown below (Fig 106):

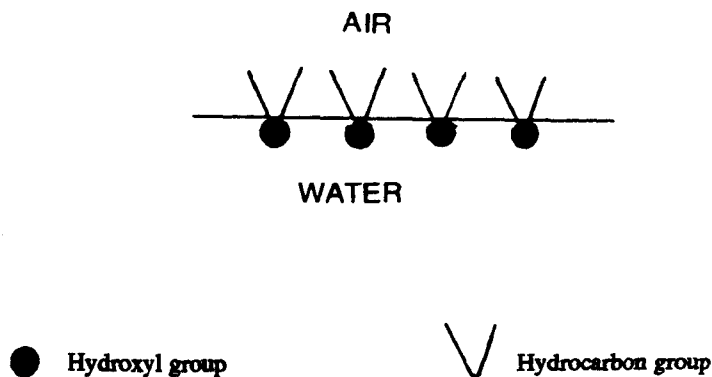


Fig 106 The orientation of propan-2-ol (IPA) molecules in water

Given the surface activity of IPA, the following situation may apply at the IPA solution/varnish interface (Fig 107):

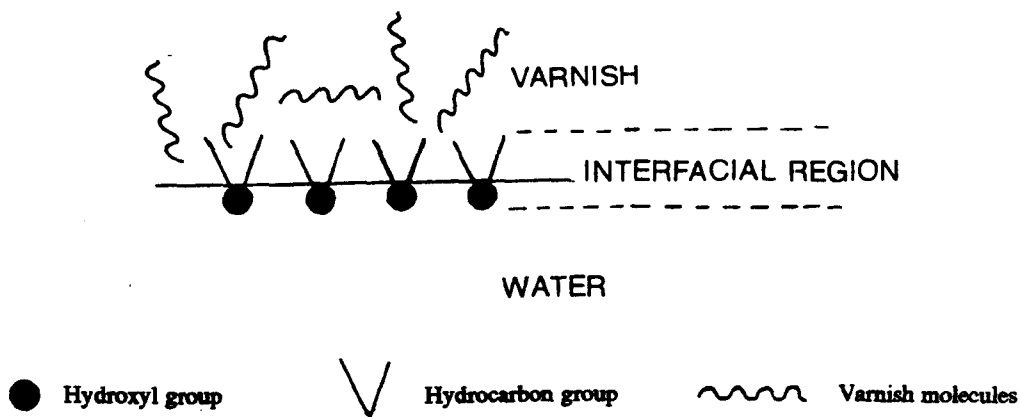


Fig. 107 Proposed situation at the IPA solution/varnish interface

In order to progress with this line of discussion, the question must be addressed as to how the IPA is distributed between the varnish and water. If the IPA is located within the

varnish, no new feature is involved beyond those already discussed earlier. If the IPA is located in the aqueous phase, this draws attention to the viscosity gradients in the region of the interface. The discussion makes the reasonable assumption that the IPA is essentially in the aqueous phase and is concentrated at the water/varnish interface⁵.

It is proposed that the rheology in the region of the fountain solution/varnish interface is affected by the surface activity of the propan-2-ol molecule. The similar hydrophobic nature of the varnish hydrocarbons and the hydrocarbon groups of the propan-2-ol molecules could result in a reduction in the amount of friction (or the viscous forces) generated during the dispersion process. Therefore, it would be expected that such a decrease in the viscous forces at the interface would inhibit the extent of droplet breakdown⁶³.

Comparing the above situation with that at the demineralised water/varnish interface where the viscosity is higher, it has been found that in the absence of IPA, where shear is applied the water droplets are broken down to a greater extent. The situation at the demineralised water/varnish interface is shown below (Fig 108).

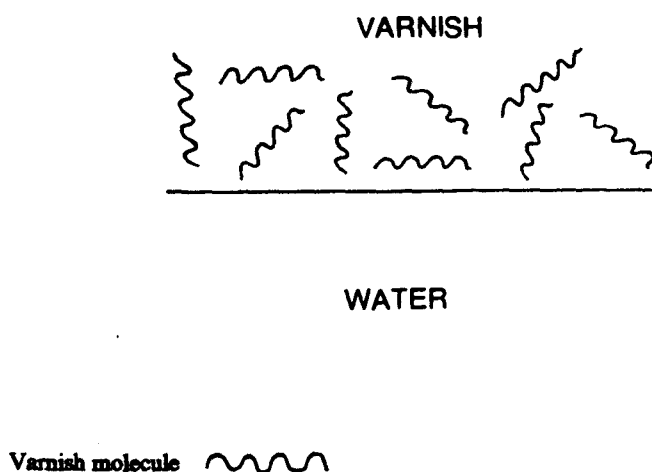


Fig 108 Proposed situation at the demineralised water/varnish interface

In the absence of IPA, the rheology at this interface is such that the gradient of viscous force is greater where shear is applied.

Consider a cube of height h_0 consisting of infinitely thin parallel layers of material (Fig 109). Assuming that the material behaves as an elastic solid, if a force F is applied to the uppermost layer in the x direction, while the lower layer remains stationary, there would be a gradient of deformation with the degree of deformation decreasing as h_i (the height of individual layers) approaches zero. It could also be said that the effective shear stress decreases as h_i approaches zero.

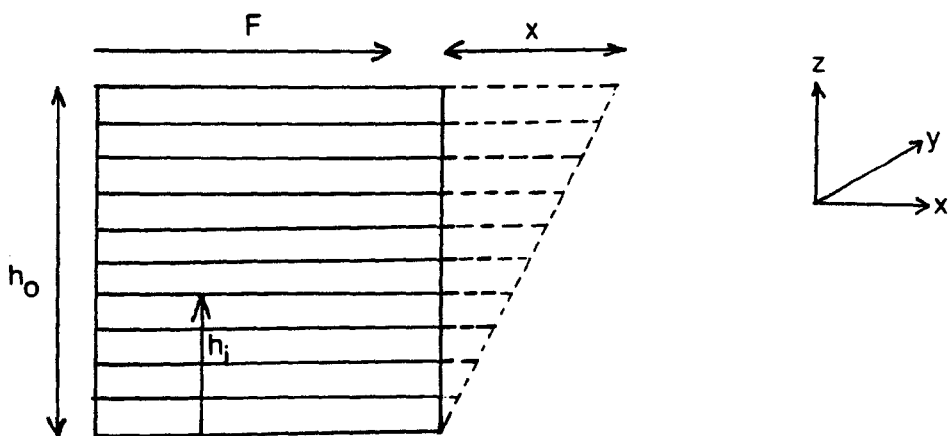


Fig 109 The deformation of a cube on the application of a force F

Similarly, if the height of the cube h_0 is increased for the same applied shear stress, it would be expected that the deformation at the lower layer would be reduced as the effective force diminishes as h_i approaches zero.

The addition of IPA to the system effectively increases the thickness of the interfacial region defined by the two phases. Applying the above theory, it would be predicted that an increase in the thickness of the interfacial region (due to the addition of IPA) would reduce the degree of deformation of the fountain solution/varnish interface. This is

illustrated in Fig 110. The effective shear stress diminishes as it approaches the interfacial region.

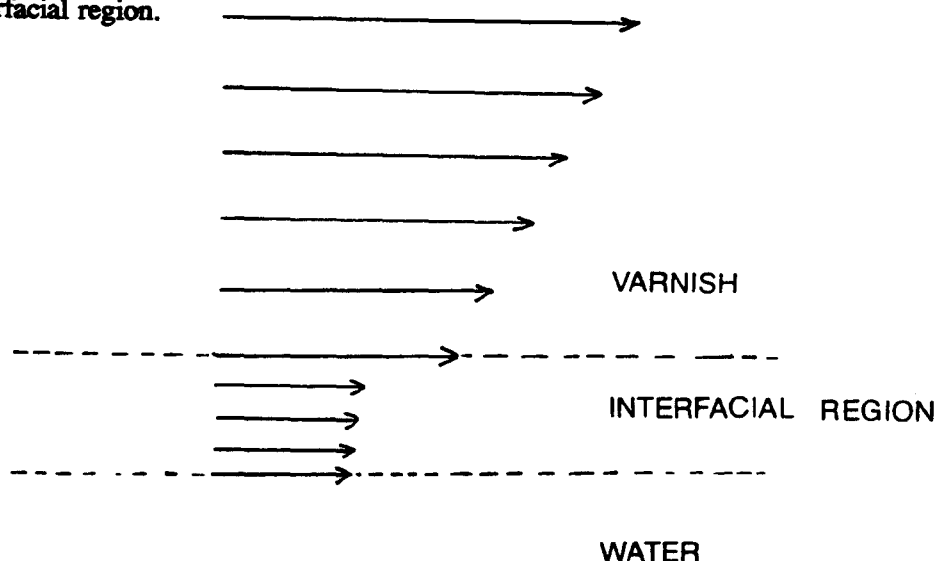


Fig 110 Proposed shear stress gradient at the IPA solution/varnish interface

Conversely, the interfacial region between the demineralised water and the varnish would be smaller than that of the system containing IPA. Applying the same theory to this system, it would be expected that a decrease in the thickness of the interfacial region (i.e. relative to that of the system containing IPA) would increase the degree of deformation of the interface (Fig 111).

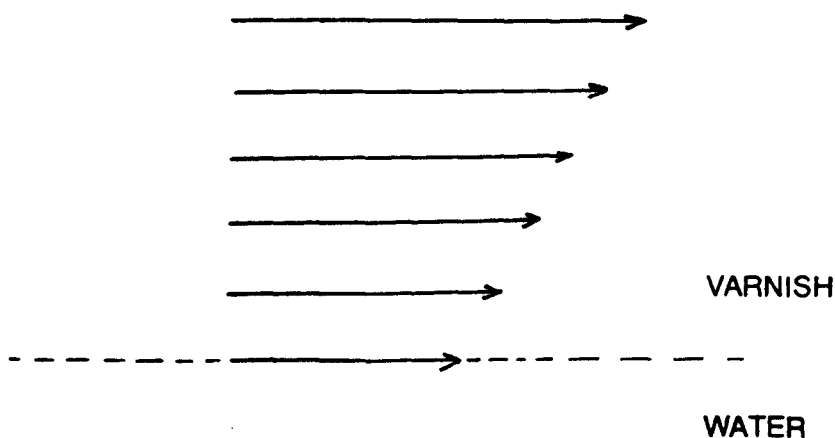


Fig 111 Proposed shear stress gradient at the water/varnish interface

Given that the deformation of a droplet is essential to the emulsification process, the breakdown of droplets under the above conditions is considered. The deformation of a droplet results in an increase in the interfacial surface area and localised thinning of the interface^{3,77}. These thinner regions are vulnerable to cleavage and therefore smaller droplets can be formed at these areas. If a surface active material is present, it may be able to migrate to the thinner regions of the interface and stabilise them (i.e. Marangoni effect)⁷⁸. This prevents further breakdown of the droplet. Under such conditions it would be assumed that surface active materials are contained within the continuous phase (according to Bancroft's rule) and 'free' surfactants can be adsorbed onto the interface thus stabilising the droplet. The IPA is dissolved in the disperse phase and this will be discussed below.

For emulsification to take place, the interface between the two phases must be disrupted by external forces. These external forces must be sufficient to overcome the Laplace pressure which opposes the breakdown of the droplets⁶³. In these studies, the viscosity differential and consequently the viscous stress forces are dominant in the process of droplet breakdown in the fountain solution/model varnish systems.

If the extent of deformation of the IPA solution/varnish interface is less than that of the demineralised water/varnish interface, the system containing IPA would be expected to produce larger droplets. This may explain why the systems containing IPA produced emulsions which had fewer droplets below 2 μm in diameter in the low shear rate mixing system. The observation that these low shear rate effects were only apparent after the fourth minute of stirring and that these effects were most prominent for droplets below 2 μm is of interest.

The limiting factor in the breakdown of droplets in any emulsification process is the radius of curvature within a specified system. The curvature increases with decreasing droplet size and therefore the smaller droplets will require a greater amount of force in order to be disrupted. This greater force may be supplied by increasing the speed of

stirring; comparing the droplet sizes between the high shear rate stirring and the low shear rate stirring experiments it can be seen that after 5 minutes of stirring, the maximum droplet diameter was approximately $6\text{ }\mu\text{m}$ at 9000 rpm whereas at 900 rpm the maximum droplet diameter was approximately $18\text{ }\mu\text{m}$. Clearly, since the stirring speed within a given series of experiments was kept constant, the differences between the droplet sizes of the systems is not due to changes in speed. The underlying mechanisms of droplet breakdown appear to be similar, irrespective of the agitation speed.

In the low shear rate studies, it is possible that the effects of IPA were only apparent after the fourth minute of stirring because it was only after this period that the droplets had reached the size where the radius of curvature was more critical. If the rheology of the interface is altered as proposed above, and the effective viscous stress at the interface is reduced due to the presence of IPA, one would expect that formation of the smaller droplets would be inhibited.

Further evidence for this is provided by the results obtained at high shear rates. Under these conditions, the differences between the droplet size distributions of systems with and without IPA were even more pronounced. The 'critical' droplet size is where droplet breakdown appears to become dependent on an effective viscous force. This is reached more rapidly as a result of the increased stirring speed. Irrespective of the speed, after 5 minutes of stirring, the reduction in the number of droplets formed below $2\text{ }\mu\text{m}$ in diameter (due to the presence of IPA) persists.

A further possible explanation, the migration of surfactant moieties (i.e. the Marangoni effect) is considered.

It is possible that Marangoni effects do occur and that propan-2-ol molecules are able to migrate within the water in order to stabilise the interface. However, it is unlikely that surfactant moieties within the varnish will be able to move quickly enough to become orientated at the interface. Moreover, given that supplies of propan-2-ol are unlikely to

be available in the continuous phase, the Marangoni effects will not be sufficient to prevent droplet breakdown if the droplet is at or above some critical diameter. This conclusion is supported by the present studies. Comparing Figs 92 and 93 it can be seen that there is a greater number of droplets above 2 μm in diameter where IPA has been added.

It has been shown that the proposed mechanism for the role of IPA in the breakdown of droplets can be correlated with existing theory.

Given the current concern over the use of volatile organic compounds (VOC), it is possible that the use of IPA will become increasingly subject to restrictions⁷⁹. In order to find suitable replacements for IPA it is important that a greater understanding of its role in the emulsification process is attained. At the same time, it must be recalled that the useful role of IPA appears to depend on its selective evaporation at suitable stages in the printing press.

In view of the findings of this study, it is recommended that the surface rheology of the fountain solution/varnish interface needs continued investigation in order to establish the further criteria required for an improved replacement for IPA.

IV SUMMARY AND CONCLUSIONS

7. Summary

The aim of this study was to examine the ink and water interactions relative to the lithographic printing process. A major technique for studying these interactions throughout the printing industry has been the Surland emulsification test method. The Surland method attempts to predict the behaviour of various combinations of inks and fountain solutions on the printing press. This well-documented method was used as a suitable starting point for this study^{32,33}.

The Surland test, which was adapted for smaller quantities of ink or varnish, has been studied in detail using model varnish and ink formulations. The limitations of this technique are illustrated by its failure to distinguish clearly between the behaviour of the hydrophilic and the hydrophobic model varnish and ink systems.

Whereas the rate and quantity of water absorption by an ink are important to its overall performance other aspects of the emulsification process needed to be examined. The present study has shown that ink/water interactions are influenced by the following factors:

- i) The rheology of water/model materials emulsions
- ii) The size and distributions of the water droplets
- iii) The 'microscopic structure' aspects (i.e. those factors influenced by time-dependency e.g. droplet breakdown and coalescence)

The latter consideration (iii) should contribute to a theoretical model to account for factors (i) and (ii). However, all of these factors are influenced by the viscosity and hydrophobicity of the continuous phase.

The rheological studies (particularly the flow experiments) showed that there was a difference in the behaviour of the model varnish systems. Slippage occurs at higher shear rates where phase redistribution in the emulsion results in the formation of a film of water on the surface of the ink or varnish layer⁸⁴. The hydrophobic systems interacted with water to produce emulsions in which a large degree of slippage was found compared with the hydrophilic systems. It became clear that the rheological behaviour, of the fluids participating in the emulsification process, was of significance in fully characterising the interactions of an ink and fountain solution. The fact that differences in the behaviour of the emulsions were observed raised the question of how the water was dispersed within the hydrophobic and hydrophilic systems.

Examination of the droplet size distributions of the emulsions showed that the hydrophilic varnish produced emulsions with a lower mean droplet size in comparison with the hydrophobic varnish.

Varying the conditions of emulsification (i.e. by changing the temperature and stirring speeds) illustrated that the extent of droplet breakdown and indeed the rate of coalescence were dictated by the specific sets of rheological conditions.

This can be shown by the fact that each emulsion prepared under different conditions was found to be approaching a different dynamic equilibrium. For example, the mean droplet diameter of the demineralised water/hydrophilic varnish emulsion at 40°C was found to be approximately 5 μm compared with 20 μm at 70°C. The change in viscosity over this temperature range for the hydrophilic varnish was found to be 300-5 Pas respectively.

An investigation of the memory or time-dependent effects found that applying a 'rest period' - which varied in length - during the emulsification process altered the apparent rate and extent of droplet breakdown.

In view of such time-dependent effects, the validity of the Surland method can now be re-examined and the basis for its use of intermittent periods of stirring evaluated.

Consider the situation in the printing process. The ink is subjected to a non-continuous shearing which occurs only in the region of the nip (i.e. near the nip entrance, nip exit and in the nip region). This shearing will change in direction to elongational shear as the ink emerges from the nip exit⁸⁰⁻⁸².

Pangalos et al ¹⁹ found that the transient response of model lithographic news inks was altered when different 'rest periods' and bi-directional shear were applied. They reported a renewal of the thixotropic response or viscosity of the ink when shearing recommenced under the above conditions. Given that the rheological properties of the varnish have been found to affect the emulsification process, the Surland method can be discussed in the context of the work of Pangalos et al¹⁹ and the present findings.

Clearly, the rate of droplet breakdown will progressively decrease during the forward sweep or positive half of the thixotropic cycle; and increase again after the downward sweep or recovery half of the cycle. The rate of coalescence of any water dispersed within the system will vary in the opposite direction.

Surland's 'ideal' P-curve appears to have taken into account the fact that a particular set of rheological conditions is necessary for good emulsification characteristics. These conditions favour a varnish or ink which initially absorbs water quickly, reaching an equilibrium after about 4 minutes of testing.

7.1 Why does the Surland Test fail ?

Given that there is a theoretical basis for the principles of the Surland method, why does it sometimes fail?

It has been said that a primary reason for the failure of the Surland method has been that the stirring mechanism does not adequately represent the emulsification behaviour of the press³⁵. However, it has also been proposed that the interfacial turbulence in the bulk content of fountain solution/ink emulsion is vastly magnified by the ink film splitting and mixing motions of the printing process. Looked at in more detail, the molecular orientations of the varnish are affected differently in the exit region of the nip than in the stirring conditions of the Surland-type emulsification test. Such differences may be at the root of the predictive failures of the Surland test. Under press conditions, the emulsification process involves elongational shear stresses which are not fully explored under the conditions of the Surland test.

The use of low shear rates in the Surland test has also been criticised. However, if increasing the shear rates applied during the emulsification process simply magnifies the breakdown of droplets, the Surland test would be expected to give some indication of the processes occurring at higher shear rates. It was found that at higher mixing speeds (i.e. at 9000 rpm) the hydrophilic varnish formed emulsions where the maximum droplet diameter was approximately 5 μm . By comparison, at low shear rates, the maximum droplet diameter was approximately 20 μm . Thus, the experiments concerning the high and low shear rate mixing provide some evidence in support of this view.

The fact that the Surland method can sometimes predict the emulsification behaviour of an ink on the press suggests that the failures of the test are not simply due to the low shear rates used.

Another possible source of the discrepancies between the Surland method and press performance might arise because the test does not take into account the temperature changes which occur during the printing process. The present study has shown changes in temperature (and consequently viscosity) affect the emulsification of the model varnish systems.

Generally, the test is carried out at room temperature or under the standard industrial conditions of 23°C at a low shear rate. Under these conditions, the mixing of the varnish or ink system may not generate enough heat to alter the viscosity significantly. However, stirring the neat varnish at room temperature (i.e. 21°C) at 9000 rpm resulted in an increase in temperature to 60°C after 35 seconds. Additionally, the opportunities for coalescence are also greatly reduced because of the higher viscosity and the lower agitation speeds⁶¹.

Changes in temperature, accompanied by changes in viscosity, affect the distribution of droplet sizes in the emulsion. Emulsification studies showed that all the model systems (i.e. hydrophilic, hydrophobic and LTHS) formed finer droplets at 40°C compared with those obtained at 70°C. These results are supported by the high speed stirring experiments where an emulsion was subjected to cycling between different temperatures.

On a press, changes in temperature occur throughout the printing process. Therefore, any test to predict or examine the behaviour of various ink and fountain solution combinations should take account of this.

7.2 A new evaluation for the validity of the Surland method

Having discussed the possible reasons for the failure of the Surland method, the fact that the test can be used successfully can now be addressed within the context of the present study. It seems reasonable that the Surland method may be valid for ink and varnish systems in which the viscosity is not affected significantly by temperature changes; and

also where the molecular orientation effects are not significantly dependent on shear directions.

The conditions for ink/water balance may also be evaluated with reference to the observed viscosity effects. A high viscosity ink, which is not affected significantly by temperature changes, should be able to produce a well-dispersed emulsion which quickly reaches a dynamic equilibrium. However, it must be noted that the rheology of such an ink must still provide suitable flow characteristics to enable it to be distributed properly and transported through the roller system.

A further restriction on the viscosity occurs as a good ink/water balance requires that a certain amount of coalescence should take place. Thus, a high viscosity continuous phase will restrict coalescence because the drainage of the film between colliding droplets will not occur at a sufficient rate to allow coalescence^{69,77}. MacPhee²³, Zang⁸⁴ and Rosenberg⁴¹ have highlighted the importance of coalescence in lithography. It is necessary for the ink to release water in the form of surface water which then serves to keep the non-image areas of the plate free of ink.

It has been shown that an ink which has high viscosity will form emulsions with finely dispersed droplets. In a colloidal system, the smaller the dispersed droplets, the greater the stability of the system. Therefore, it may be inferred from the models proposed by MacPhee²³ and Zang⁸⁴ that emulsions produced in lithography operate on the edge of instability to enable the formation of surface water.

If a high viscosity ink forms a stable emulsion, consider the effects of the hydrophobicity of the model varnish. The results show that irrespective of the shear rate, the hydrophobic varnish produces larger droplets than the hydrophilic varnish; this distinction can be made by reference to the experiments at 70°C, where the viscosity of both varnishes is virtually identical. This indicates that the hydrophobicity of the varnish will affect the emulsification process. According to the theories of emulsion stability, polar

droplets dispersed within a hydrophobic system will minimise the interfacial area, i.e. they will form dispersions with a low surface to volume ratio. Given that both these varnishes are hydrophobic relative to water, it would be expected that the *less* hydrophobic varnish should form emulsions with a greater number of small droplets; under conditions where viscosity, temperature and shear rates are comparable.

Thus, returning to MacPhee's model, it may be inferred that the most suitable ink for lithography should be as hydrophobic as possible, while still allowing emulsification with the fountain solution. The high viscosity would ensure that the fountain solution would be absorbed and emulsified quickly, while the increased hydrophobicity would allow coalescence and the production of surface water.

7.3 Conclusions

Having carried out a detailed study of the emulsification characteristics of the fountain solution/model varnish and ink systems, it was found that the rheology of the continuous phase plays a major role in determining the type of emulsion formed. The key processes affected by the rheology are:

- i) fragmentation of droplets
- ii) coalescence of droplets
- iii) elastic recovery and time-dependency
- iv) nature of the process at the interface

Any characterisation of ink/water balance by a Surland-type test or otherwise should be supplemented by information from the above processes.

7.4 The effects of IPA

Identifying the factors above have provided an experimental and theoretical base for addressing some of the issues concerning ink/water interactions. One of the most important of these is the role of IPA in lithography.

Rosenberg⁴¹ and Iwaki et al⁴² reported that the addition of IPA resulted in the formation of a more uniform or broader droplet distribution.

The present work has indicated that IPA affects the droplet size distribution by inhibiting the formation of droplets below 2 μm in both the low shear rate and high shear rate experiments. The proposed mechanism for this suggests that the presence of IPA alters the rheology of the fountain solution/varnish interface, thus affecting the breakdown of the droplets (section 6.5). These proposals need further investigation, particularly in the measurement of the interfacial rheology of the emulsion systems. The possibility of replacing IPA with a safer alternative, which will maintain current standards of press performance, will be improved with a greater understanding of ink/water balance phenomena.

In the light of current changes towards higher machine speeds and the trend towards shorter print runs, the development of suitable inks to make the lithographic process more efficient is a continuous requirement. It is important to ensure that the ink/water balance remains appropriate within such developments.

7.5 Future work

The addition of pigment (i.e. Cyan Lutentia, which is a phthalocyanine blue) to the varnish systems influenced the quantity of, and apparent rate at which, water was absorbed; the rheological properties of the varnish were also affected. However, the trends resulting from the differences in the hydrophobicity of the varnish were still

apparent in the pigmented systems. Although time did not allow a programme of study dedicated to the effects of various pigments, it appears that the varnish plays the key role in the dispersion of water within the pigmented and unpigmented systems. In order to validate this conclusion further tests need to be carried out on pigmented systems. It will also be desirable to evaluate emulsion samples which have been removed from a press according to the criteria established within this study. The nature and behaviour of these samples can be compared with the resulting printed materials, thus providing an improved means of equating emulsion properties with print performance.

This study has highlighted the importance of the processes at the water/varnish interface. Thus, a recent study has investigated the compression/expansion of a monolayer of resin used in the model varnish systems⁶⁷. Compression of the monolayer — which was formed on a deionised water subphase — led to the monolayer collapsing to form a multilayer. The addition of IPA to the subphase resulted in a reduction of the compression pressure at which the monolayer separated from the subphase. These observations are consistent with the reduction of interfacial rheology indicated in the present study and also the apparent 'softening' of ink by IPA reported by Dowe and Blokker²⁷. Further study of the nature of interface rheology should assist in determining suitable replacements for IPA.

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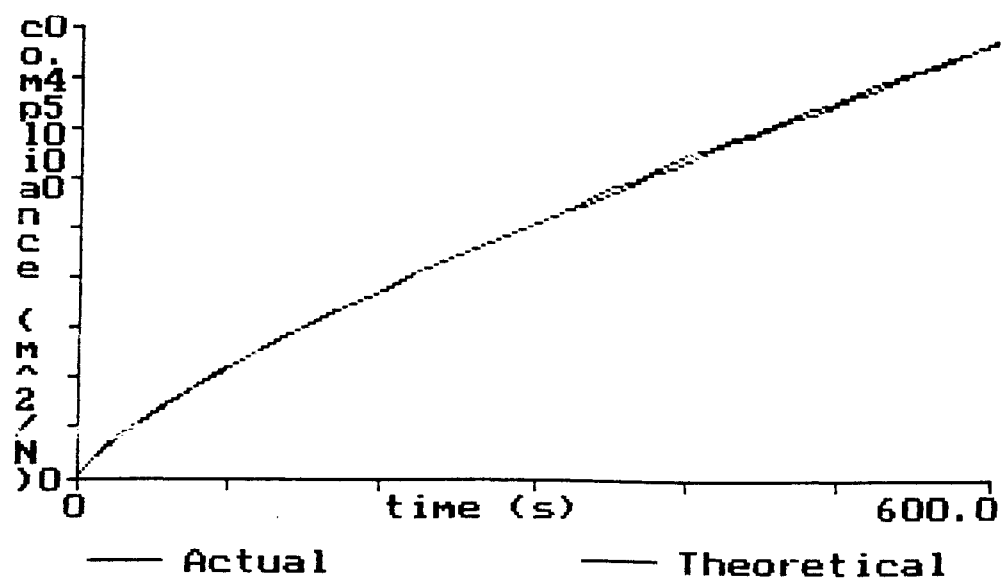
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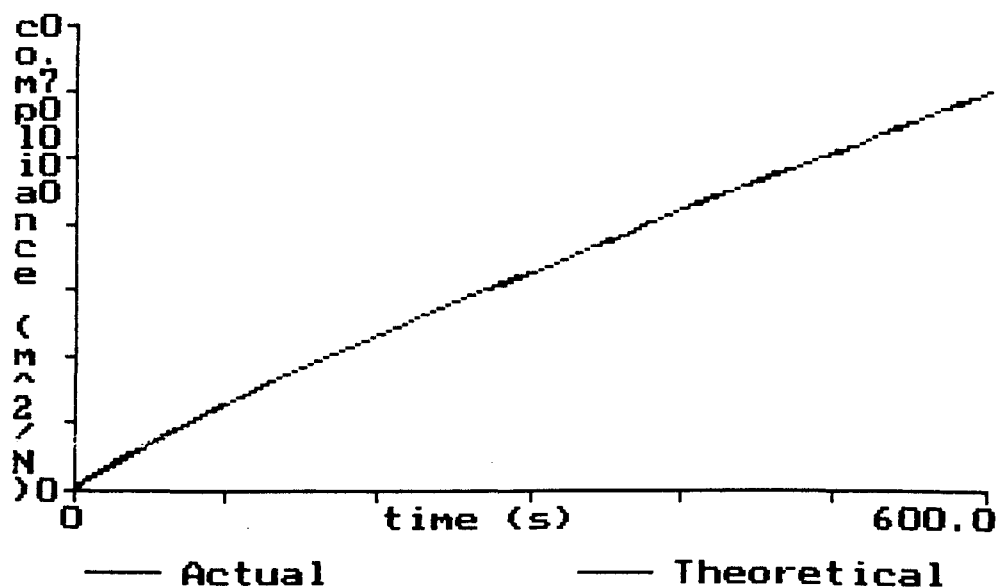
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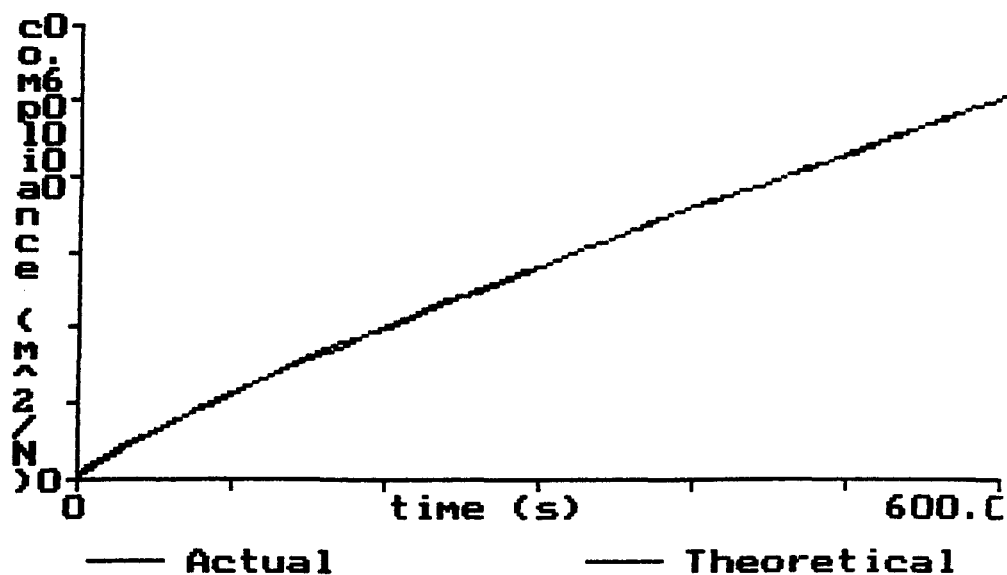
APPENDIX I



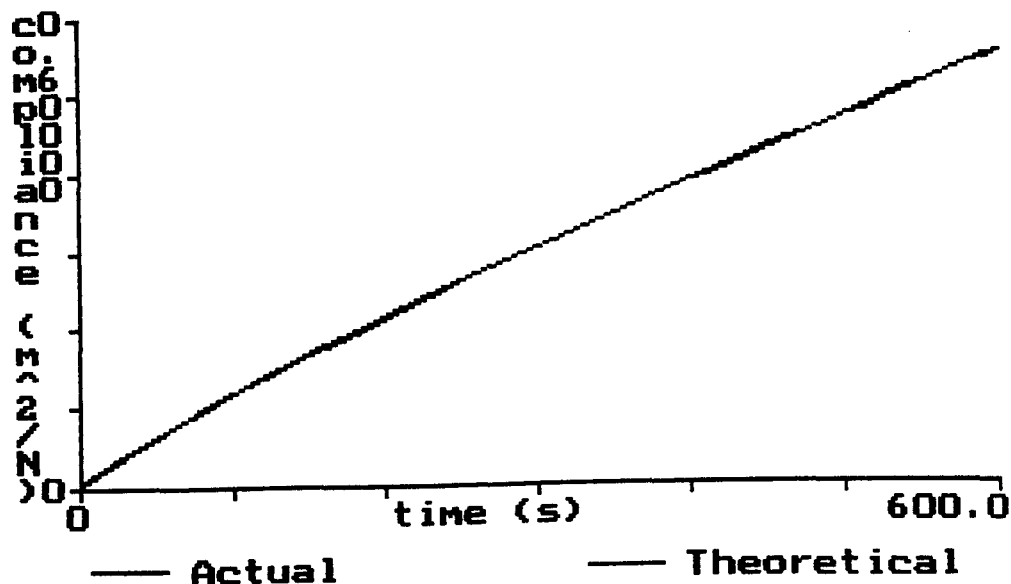
1 (a) Actual and theoretical creep curves of the hydrophobic varnish



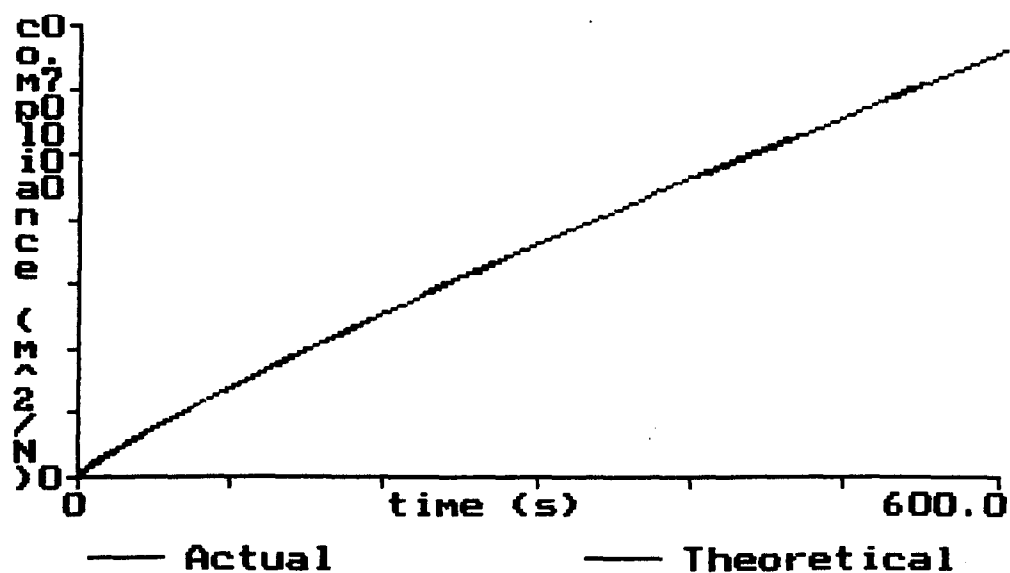
1 (b) Actual and theoretical creep curves of the hydrophobic varnish emulsion with 5% water



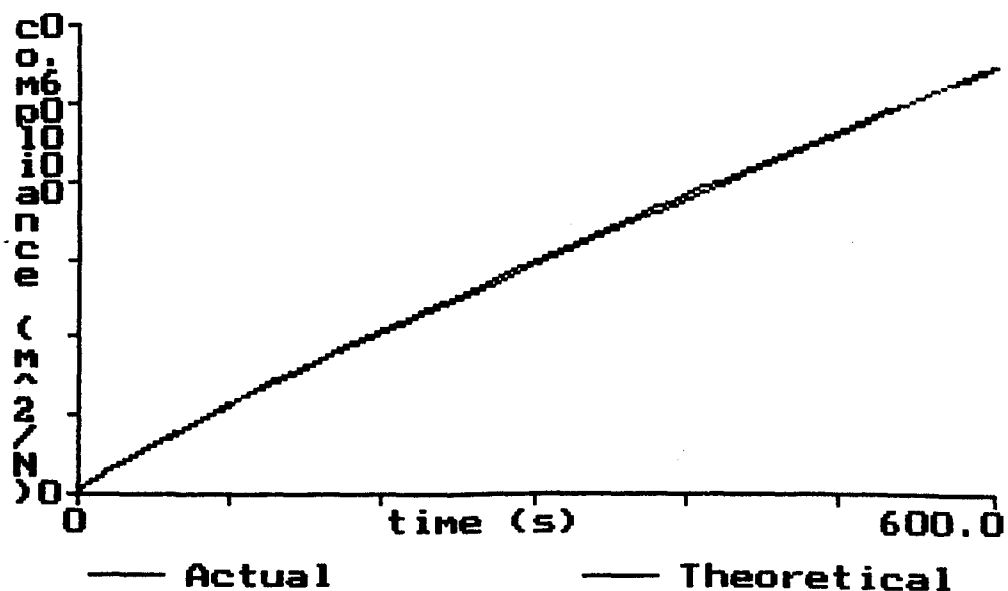
1 (c) Actual and theoretical creep curves of the hydrophobic varnish emulsion with 10% water



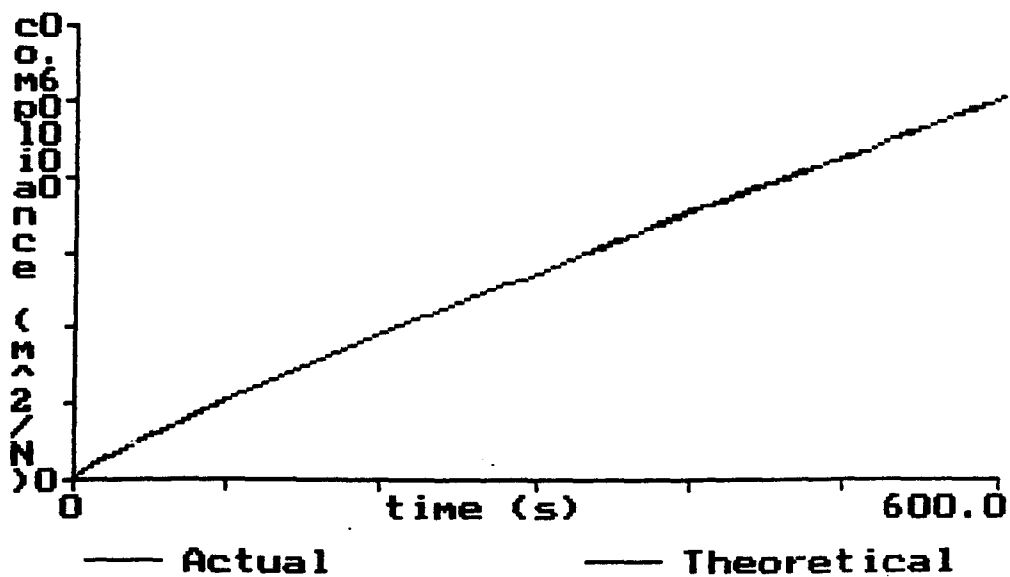
1 (d) Actual and theoretical creep curves of the hydrophobic varnish emulsion with 15% water



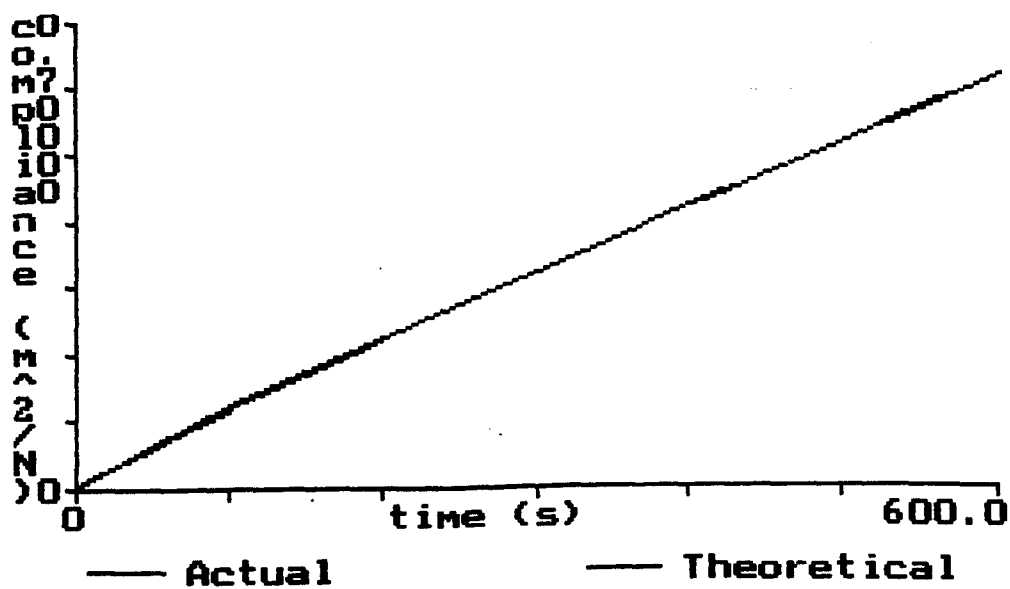
1 (e) Actual and theoretical creep curves of the hydrophobic varnish emulsion with 20% water



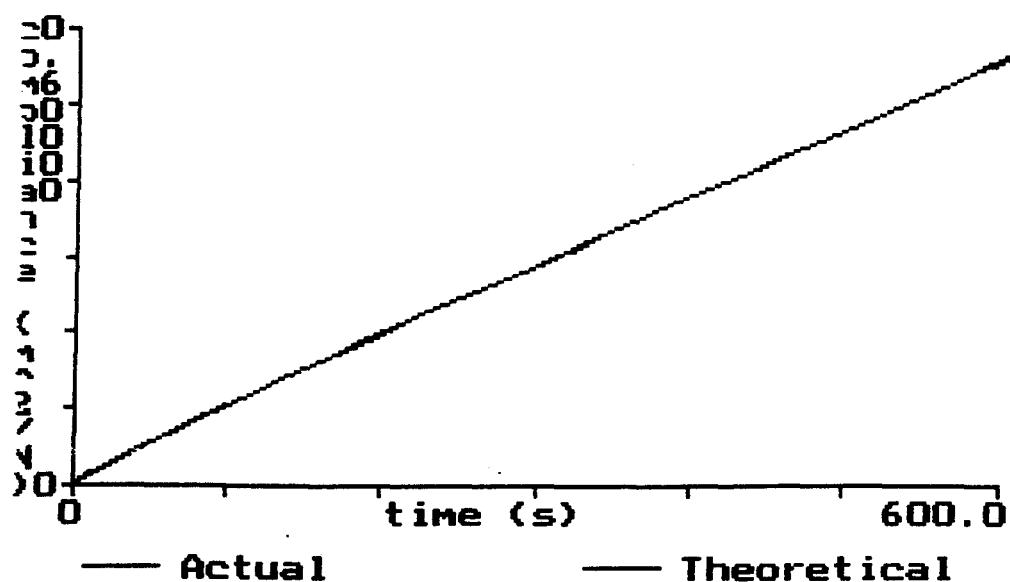
1 (f) Actual and theoretical creep curves of the hydrophobic varnish emulsion with 25% water



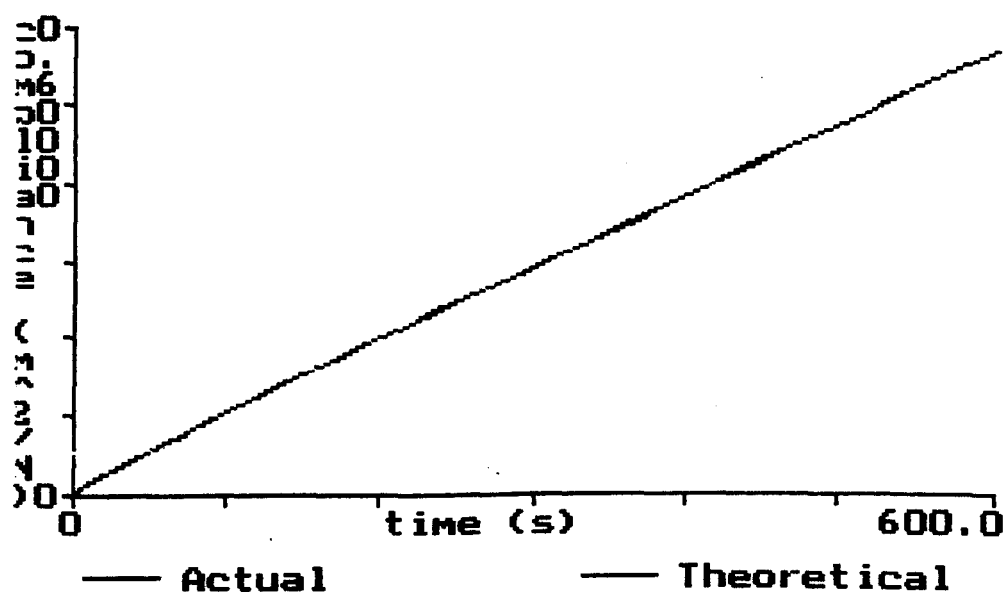
2 (a) Actual and theoretical creep curves of the hydrophilic varnish



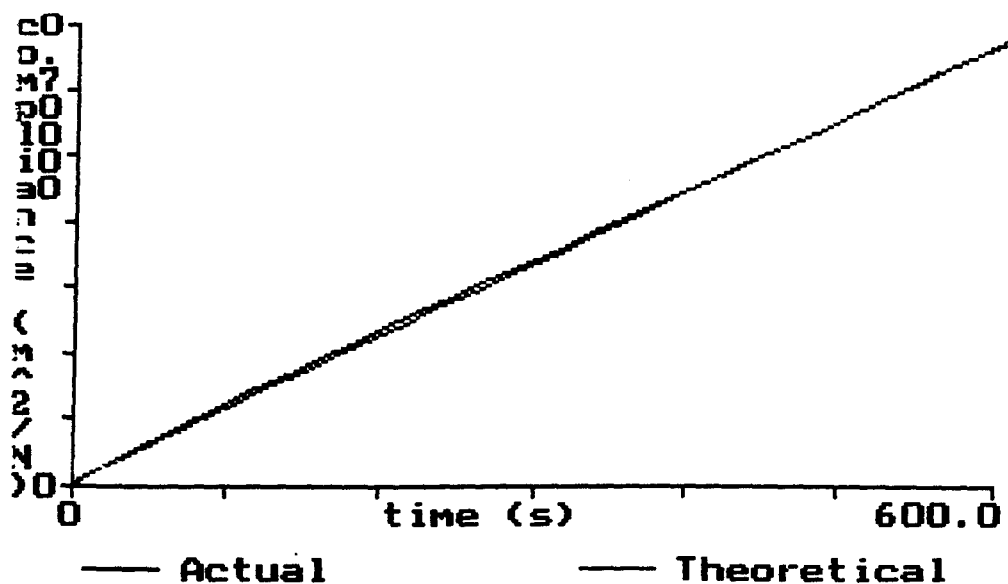
2 (b) Actual and theoretical creep curves of the hydrophilic varnish emulsion with 5% water



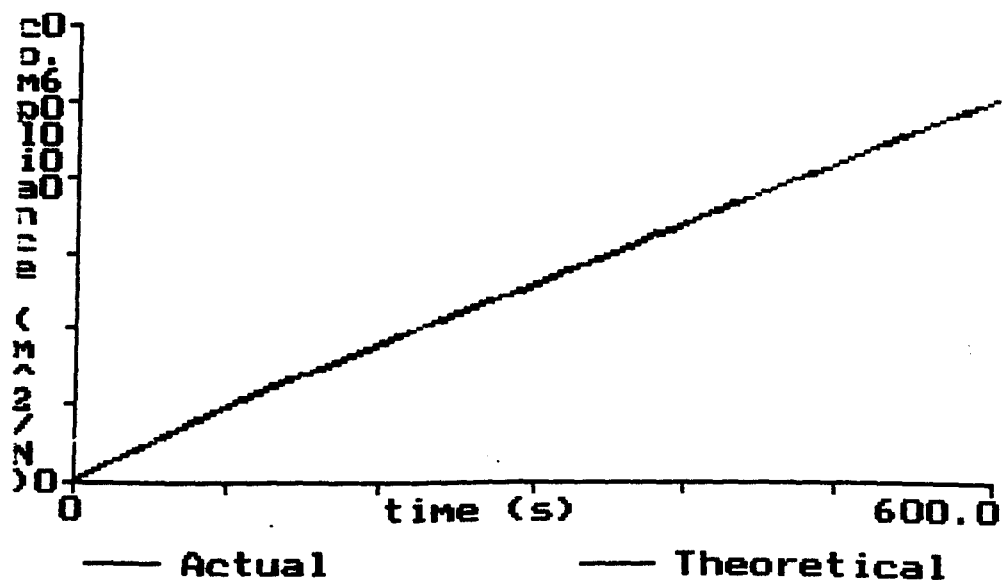
2 (c) Actual and theoretical creep curves of the hydrophilic varnish emulsion with 10% water



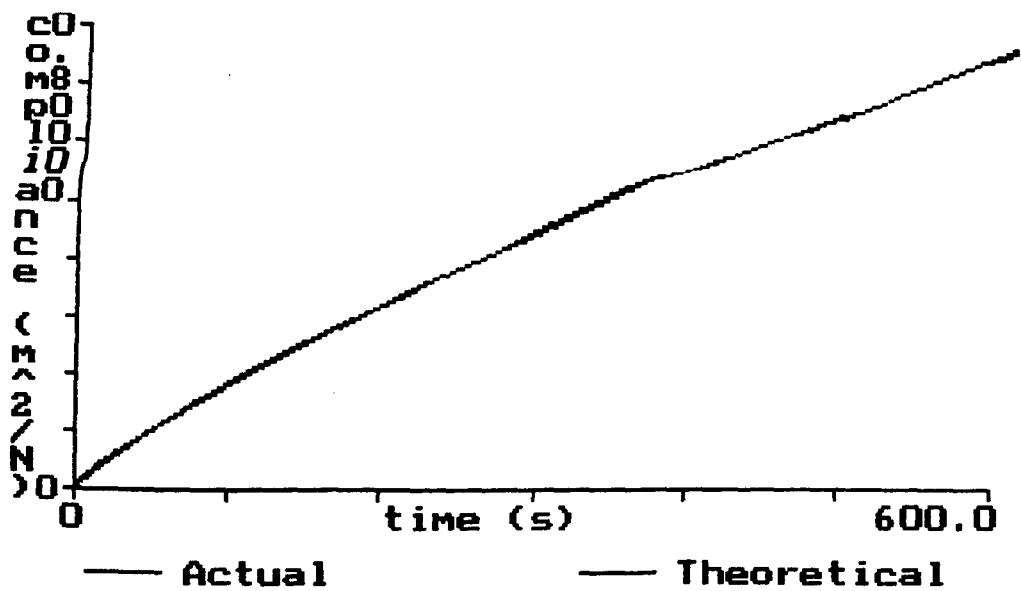
2 (d) Actual and theoretical creep curves of the hydrophilic varnish emulsion with 15% water



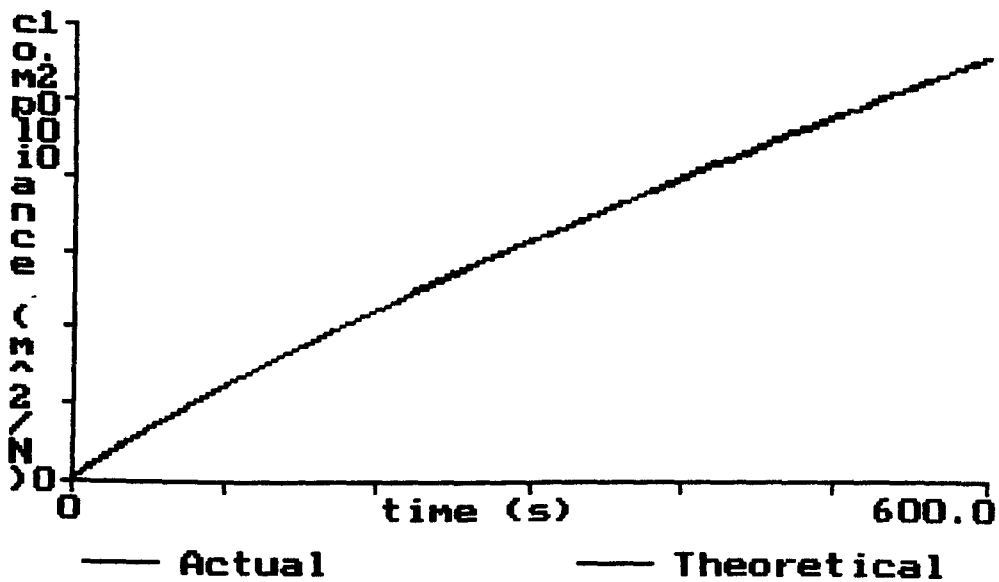
2 (e) Actual and theoretical creep curves of the hydrophilic varnish emulsion with 20% water



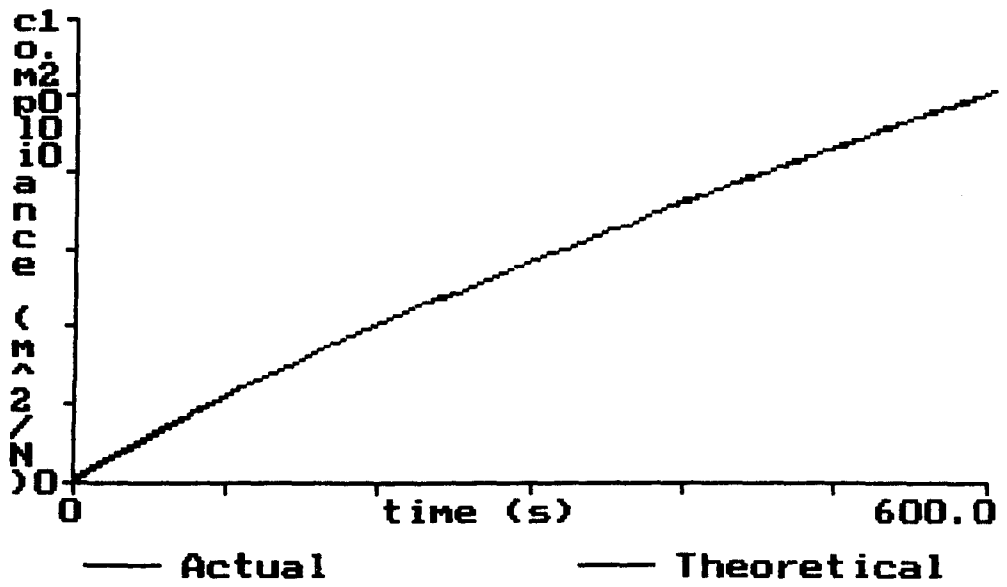
2 (f) Actual and theoretical creep curves of the hydrophilic varnish emulsion with 25% water



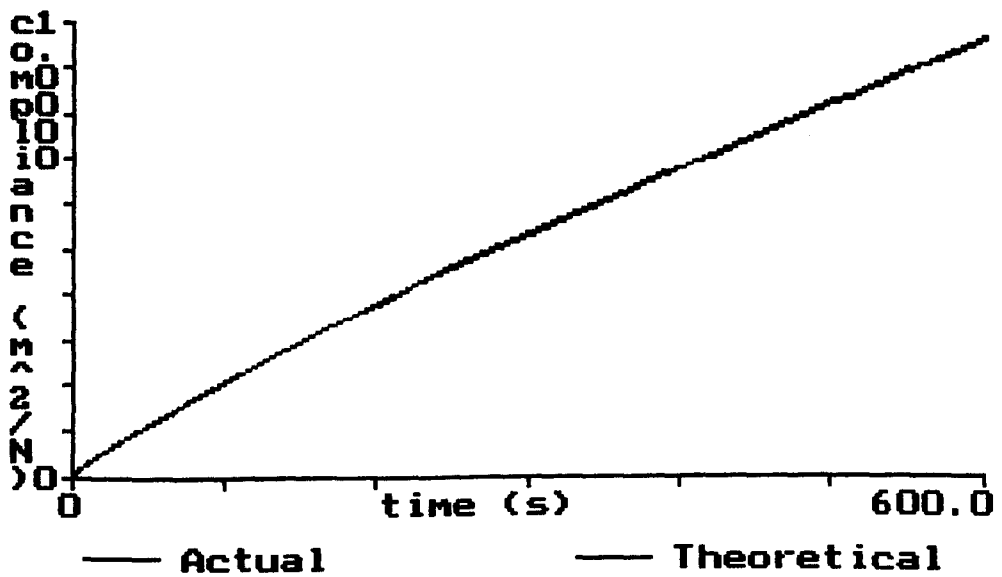
3 (a) Actual and theoretical creep curves of the hydrophobic ink



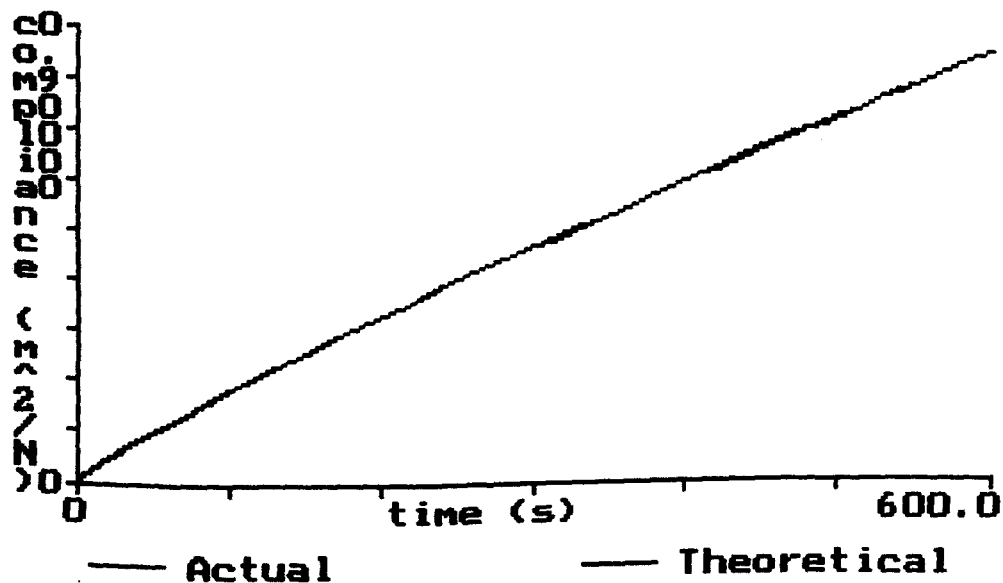
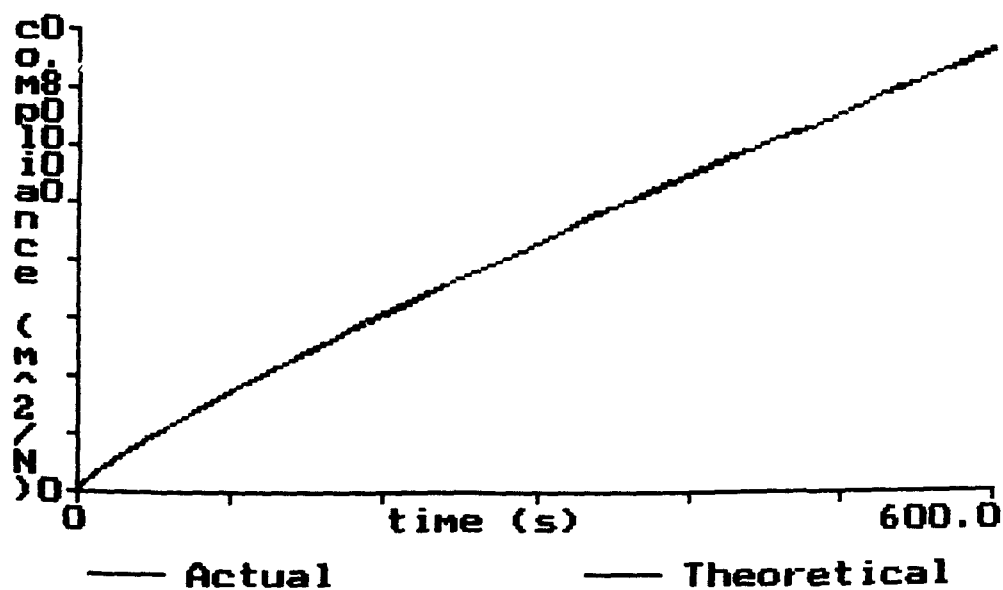
3 (b) Actual and theoretical creep curves of the hydrophobic ink emulsion with 5% water

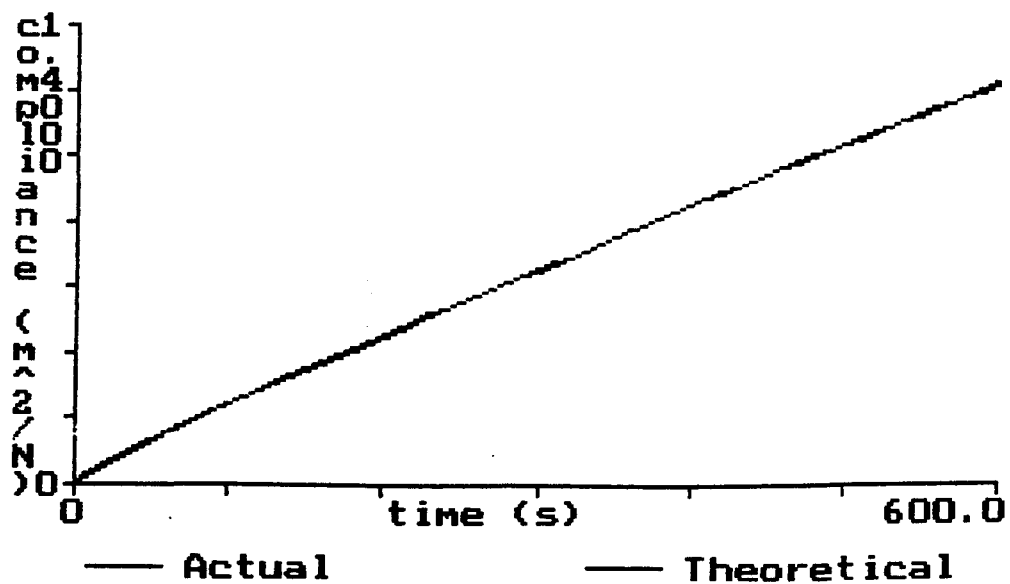


3 (c) Actual and theoretical creep curves of the hydrophobic ink emulsion with 10% water

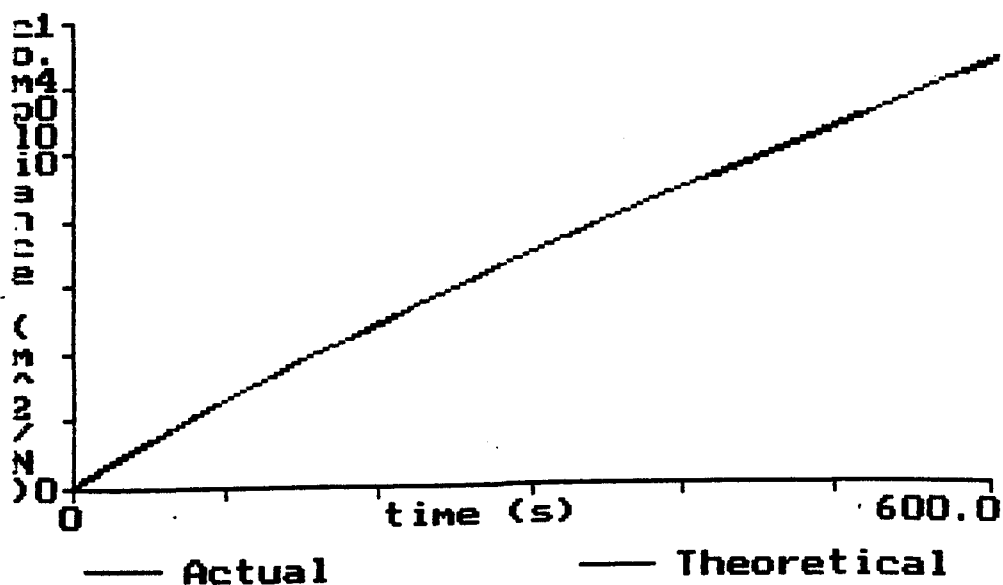


3 (d) Actual and theoretical creep curves of the hydrophobic ink emulsion with 15% water

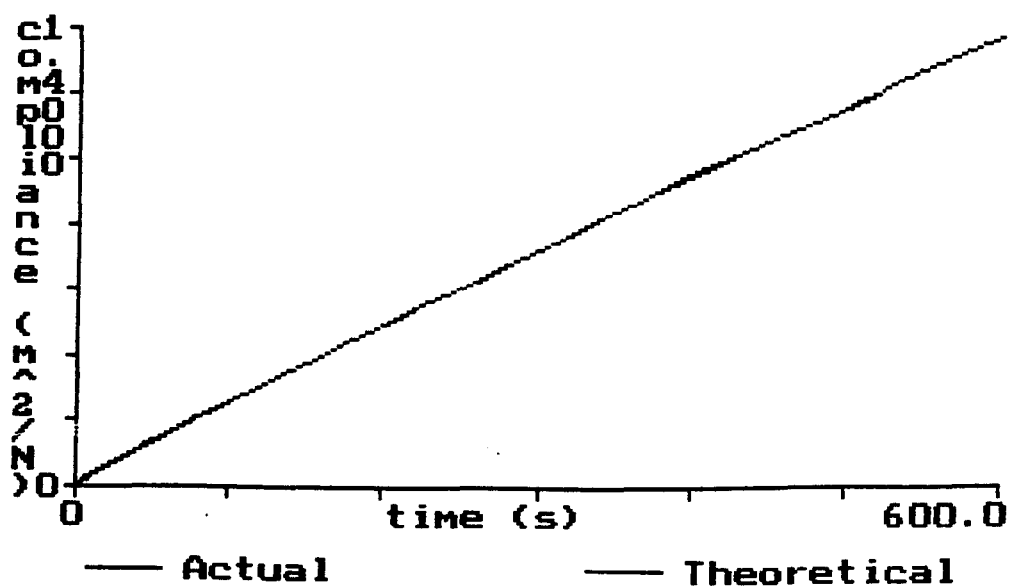




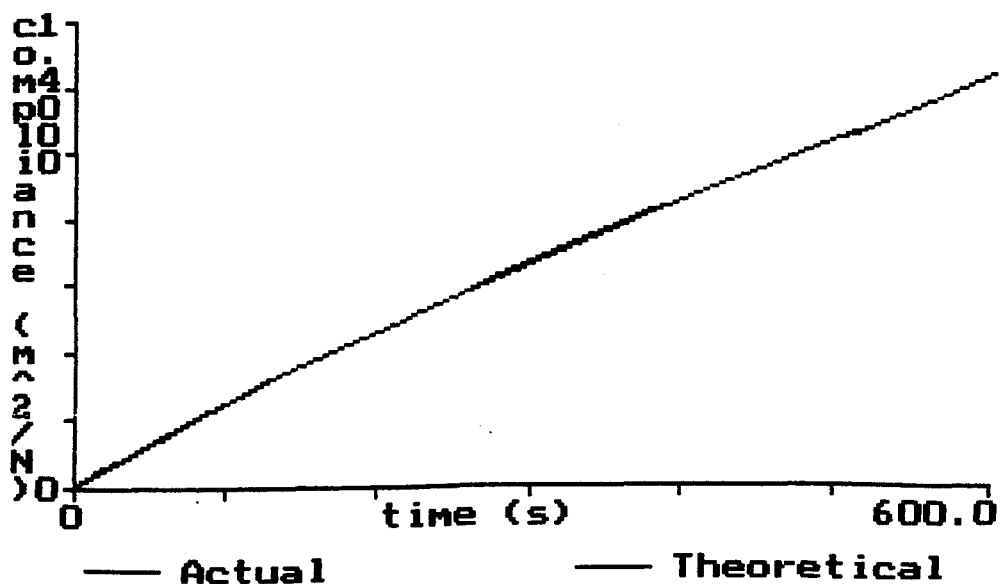
4 (a) Actual and theoretical creep curves of the hydrophilic ink



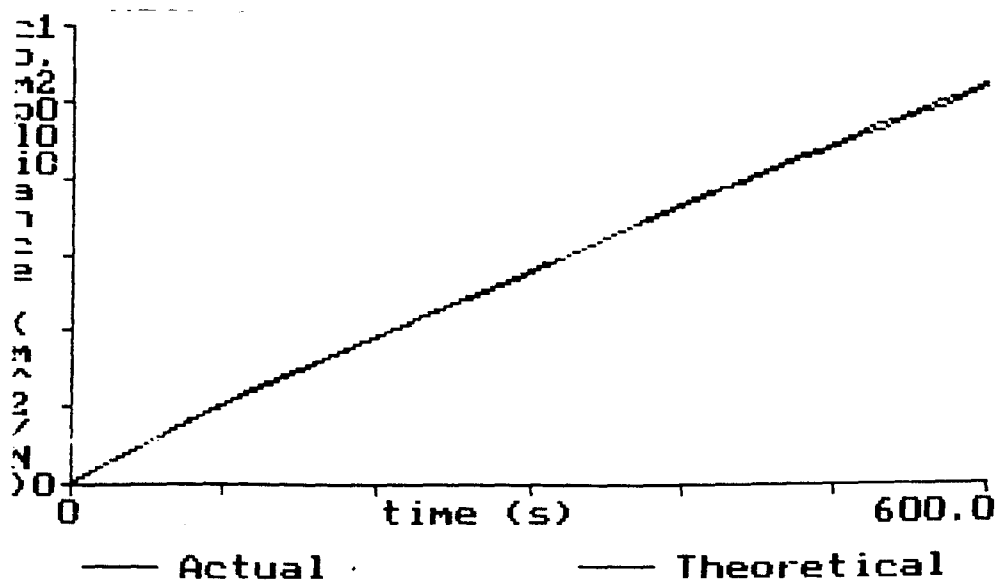
4 (b) Actual and theoretical creep curves of the hydrophobic ink emulsion with 5% water



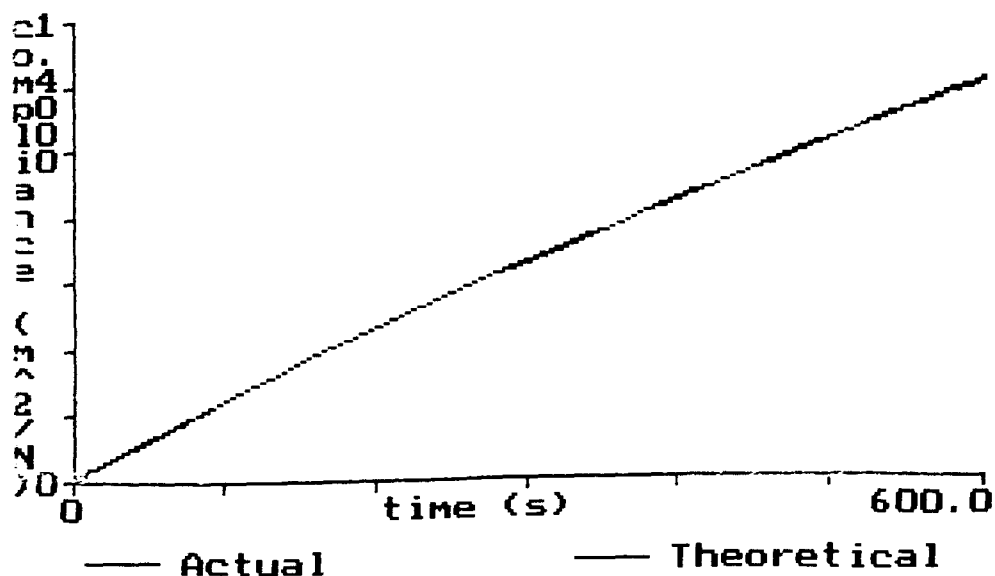
4 (c) Actual and theoretical creep curves of the hydrophilic ink emulsion with 10% water



4 (d) Actual and theoretical creep curves of the hydrophilic ink emulsion with 15% water



4 (e) Actual and theoretical creep curves of the hydrophilic ink emulsion with 20% water



4 (f) Actual and theoretical creep curves of the hydrophilic ink emulsion with 25% water